SOME STUDIES ON TRIPLE HALIDE, HYDROXIDE AND ALKOXIDE BRIDGED COMPLEXES OF RUTHENIUM(II) AND OSMIUM(II)

TERENCE ARTHUR

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My thanks to Dr.T,A.Stephenson for his enthusiastic help and to the University of Edinburgh for their financial support.

To my dear wife Alison.

Abstract.

The work in the thesis is concerned with the syntheses, structures and reactions of triple bridged binuclear complexes of ruthenium and osmium.

Chapter 1 deals with the earlier published chemistry for triply bridged complexes of these two elements and other transition metals.

Chapter 2 describes the syntheses and characterisation of some new monomeric arene complexes namely $RuX_2(\eta^6\text{-arene})py$ and $[RuX(\eta^6\text{-arene})(py)_2]PF_6$ and how these compounds react together with HBF_4 in methanol to form the triple-halo bridged complexes $[Ru_2(\mu\text{-}X)_3(\eta^6\text{-arene})_2]BF_4$ in high yields. The syntheses of heterobridged, heteroarene and heteronuclear complexes as mixtures, (as shown by ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. studies), is also described.

In chapter 3, the reactions of $[RuCl_2(\eta^6\text{-arene})]_2$ with aqueous solution of NaOH and Na_2CO_3 and alcoholic solutions of NaOR are discussed, and the isolation and characterisation of some triple hydroxo and alkoxo bridged cations ie. $[Ru_2(\mu\text{-}OR)_3(\eta^6\text{-}C_6H_6)_2]^+$ is described. Some preliminary reactions of these complexes is also included.

Chapter 4 describes the syntheses and characterisation of some new triple chloro-bridged complexes of ruthenium and osmium containing group 5B donor ligands. Thus, the reactions of the ruthenium(II)(II) binuclear compound $Ru_2(\mu\text{-}Cl_3)Cl(Y)(PR_3)_4$ (Y = CO, CS, R = Ph,p-tolyl) and $Ru_2(\mu\text{-}Cl)_3Cl(PEt_2Ph)_5$ with conc. HCl in either acetone or nitromethane leads to the formation of the mixed valence complexes $Ru_2(\mu\text{-}Cl)_3Cl_2(Y)(PR_3)_3$ and $Ru_2(\mu\text{-}Cl_3)Cl_2(PEt_2Ph)_4$ respectively.

The syntheses and reactions of $OsCl_2(PPh_3)_3$ and $OsCl_2(CO)$-

Abstract cont.

$(PPh_3)_2(solv)$ (solv. = dmf, MeOH) are also described. The reaction of $RuCl_2(PPh_3)_3$ with $OsCl_2(CO)(PPh_3)_2(MeOH)$ leads to the formation of the hetero-nuclear complex $RuOs(\mu\text{-}Cl_3)Cl(CO)(PPh_3)_4$ as shown by infra-red and $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy.

Finally some electrochemical studies on these new complexes by cyclic voltammetry and a.c. polarography are discussed.

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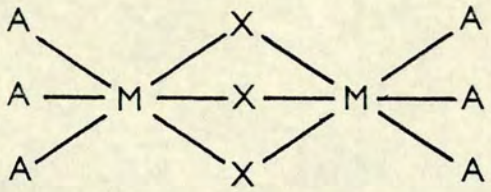
Chapter 1

The Syntheses and Reactions of Some Triply Bridged Binuclear Transition Metal Compounds

1.1 Introduction

There are many binuclear transition metal complexes having a structure (1) based on two octahedra sharing a common face.



(1)

This creates a situation where there are three bridging groups X between the metal centres M. The terminal groups A can be varied in a number of ways such that three different classes of compound can be defined.

a) When A = X = halide, the compounds are the well-known nonahalide anions.

b) When $A_3 = \eta^n\text{-}C_nR_n$, the compounds have the structure $(\eta^n\text{-}C_nR_n)M(\mu\text{-}X)_3M(\eta^n\text{-}C_nR_n)$ (R = H, alkyl); where $\eta^n\text{-}C_nR_n$ = π bonded carbocyclic rings (n = 4 to 7) and X = halide, H^-, OH^-, OR^-, SR^-, SeR^-. (R = alkyl, aryl).

c) When A = L, where L is a two electron donor ligand such as CO, PR_3; (R = alkyl, aryl), the compounds are of the type $M_2(\mu\text{-}X)_3X_nL_{(6-n)}$ (n = 0 to 5) and X = halide, H^-, OH^-, OR^-, SR^-, (R = H, alkyl).

Since the work in this thesis is concerned with the syntheses, structures and reactions of triple bridged complexes of ruthenium and osmium, it is appropriate at this juncture to discuss briefly the earlier published chemistry of these three classes of compound, for various transition elements.

1.2 The nonahalide and related anions.

The triply bridged nonahalide anions can be regarded as the first member of the general series $M_2(\mu\text{-}X)_3X_6$ to $M_2(\mu\text{-}X)_3L_6$, and it is therefore appropriate to discuss them first.

Group IV: Titanium, Zirconium and Hafnium.

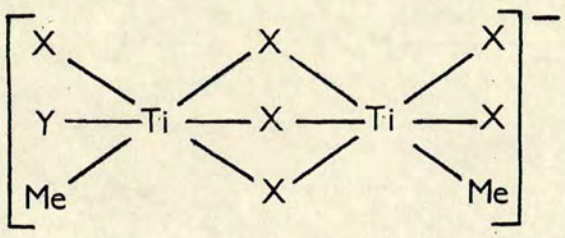
This group is dominated by the compounds of titanium with only one report of a complex of this type for zirconium[1] and none for hafnium.

There are two different series of compound, those containing formally Ti (IV) and those with Ti (III). The first report[2] of the $[Ti_2Cl_9]^-$ ion appeared in 1968, when it was isolated as the tetraethylammonium salt by dropwise addition of $[Et_4N]Cl$ in dichloromethane to $TiCl_4$ in the same solvent. The analogous bromide was prepared later[3] by the reaction of $[Et_4N]Br$ and $TiBr_4$. The formulation of these anions as binuclear species with three bridging halo groups was shown to be correct in 1971 when the X-ray structure of $PCl_4[Ti_2Cl_9]$ was determined.[4] The analogous compound $^tBuPCl_3[Zr_2Cl_9]$ was reported[1] in 1974. The $[Ti_2F_9]^-$ anion was observed[5] in 1973 during an ^{19}F n.m.r. study of the reaction of TiF_4 with the $[TiF_6]^{2-}$ dianion and it was later isolated as the caesium and the tetrafluoroammonium salts.[6] The compound $Ca[Ti_2(OEt)_9]_2$ was prepared by the reaction of $Ca(OEt)_2$ with $Ti(OEt)_4$ and shown to contain the triple ethoxo bridged anion $[Ti_2(OEt)_9]^-$ by X-ray analysis.[7] No reactions of any of these compounds have been reported.

Other Ti (IV) anions which can be included in this group are the compounds $Et_4N[Ti_2Me_2X_6Y]$ ($X = Cl^-$, $Y = Cl^-$, Br^-; $X = Br^-$, $Y = Cl^-$, Br^-) and these are made similarly to the nonahalides[3] (eqn. [1].

$$[Et_4N]Y + 2TiMeX_3 \xrightarrow{0^\circ C/CH_2Cl_2} EtN[Ti_2Me_2X_6Y] \quad ---- [1].$$

However, reaction of these compounds with excess of tetraethylammonium halide gives the dianions $(Et_4N)_2[Ti_2Me_2X_6Y_2]$ and far ir. studies suggest that the structures of the anions $[Ti_2Me_2X_6Y]^-$ (2) and $[Ti_2Me_2X_6Y_2]^{2-}$ (3) are analogous to those determined by X-ray analyses on $PCl_4[Ti_2Cl_9]$ and $[PCl_4]_2[Ti_2Cl_{10}]$ respectively.[4]



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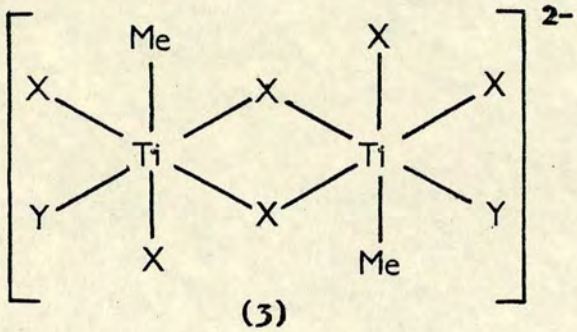
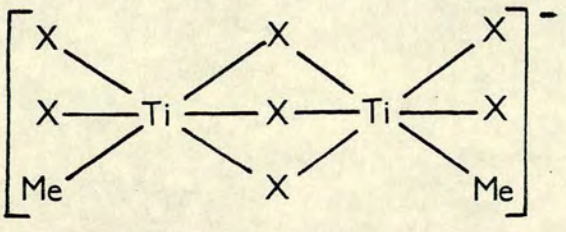


(3)

For the anions $[Ti_2Me_2X_7]^-$, there are two possible geometrical isomers (4) and (5).



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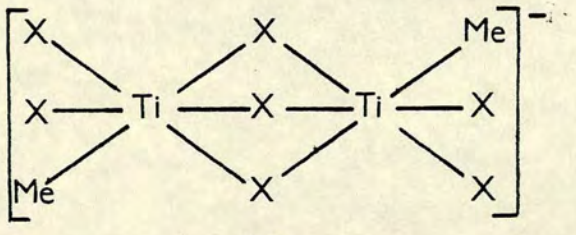

(5)

These could not be differentiated in the solid state, but were shown to be present by variable temperature ^1H n.m.r. studies.[3] Thus, at room temperature, one methyl resonance is observed in dichloromethane, whereas at $-100^\circ C$, two signals separated by only 0.05 ppm were found. A fast intramolecular exchange process at ambient temperature has been

proposed to explain these observations. For the anions $[Ti_2Me_2X_6Y]^-$, the halide Y was shown by far ir. studies to occupy a terminal position and thus, the methyl groups are no longer magnetically equivalent. However, even at -100°C with the intramolecular process mentioned above frozen out, no further splitting of the signals was observed, suggesting that the chemical shift difference between the two methyl groups is very small.

The only reported reaction of these compounds is with molecular oxygen.[3] Thus, $Et_4N[Ti_2Me_2Cl_7]$ reacts with oxygen with insertion into the metal carbon bond to give the corresponding methoxy - derivative $Et_4N[Ti_2(OMe)_2Cl_7]$.

The Ti (III) binuclear anion $[Ti_2Cl_9]^{3-}$ will be discussed later in conjunction with the $[M_2Cl_9]^{3-}$ anions (M = Cr, Mo, W) with which it has more in common.[8]

Group V: Vanadium, Niobium and Tantalum.

Only the chlorides of vanadium (III)[9,10] and niobium (III)[11] have been reported to date. For example the niobium (III) compounds $M'_3[Nb_2Cl_9]$ ($M' = Cs^+$, Rb^+) were prepared[11] by the high temperature reaction of caesium or rubidium chloride with Nb_3Cl_8 and $Cs_3[V_2Cl_9]$ was prepared similarly.[9] The reaction[10] of VCl_3 with $[Et_4N]Cl$ in thionyl chloride gives $(Et_4N)_3[V_2Cl_9]$. No reactions of these complexes have yet been reported.

Group VI: Chromium, Molybdenum and Tungsten.

This is by far the most investigated group of compounds and there are many synthetic routes to various alkali metal and tetraalkylammonium salts of $[M_2X_9]^{3-}$ (M = Cr,Mo,W; X = Cl^-,Br^-). A few dianions $[M_2X_9]^{2-}$ are also known.

Chromium: The anion $[Cr_2Cl_9]^{3-}$ was first made as the caesium salt in 1957 and its structure determined by X-ray analysis.[12] It was

synthesised by fusing CsCl and $CrCl_3$ at 725°C for several days. The potassium and rubidium salts of the chloro, as well as the caesium salts of the bromo and iodo complexes were later prepared similarly,[9] and X-ray analysis[10] of $Cs_3[Cr_2Br_9]$ confirmed the confacial bioctahedral structure of the anion. Although reported,[10,14] the tetraethylammonium salt $(Et_4N)_3[Cr_2Cl_9]$ was later shown to be impure, but the pure tetra-n-butylammonium compound $(^nBu_4N)_3[Cr_2Cl_9]$ could be made by the same route.[9]

Molybdenum: The synthesis of the compounds $M'_3[Mo_2Cl_9]$ ($M' = Cs^+$, Me_3NH^+) was carried out by Nyholm et al[15] in 1969 by precipitation from strongly acidic solution on addition of M'Cl. The Et_4N^+ and Et_3NH^+ salts together with the Et_4N^+ salt of the bromo compound were reported in the same year.[16] The syntheses of the caesium salts of the chloro and bromo anions by the fusion of CsX with MoX_3 ($X = Cl^-$, Br^-) has also been reported.[17]

In 1973, Wentworth and co-workers[18] were trying to find a new synthetic route to the nonahalide anions $[M_2Cl_9]^{n-}$ (M = Mo, W; n = 2 or 3) which did not involve the rather alchemical reactions used previously. They believed that the anions $[MCl_6]^{n-}$ (n = 0, 1, 2) would serve as easily reducible, tridentate ligands which might displace carbonyl groups from the trigonal face of a metal carbonyl halide such as $[M(CO)_5Cl]^-$ or $[M(CO)_4Cl_3]^-$. Therefore, the following reaction was devised and tested for M = Mo or W (eqn. [2]).

$$[MCl_6]^{n-} + [M(CO)_4Cl_3]^- \longrightarrow [Cl_3MCl_3M(CO)Cl_3]^{(n+1)-} + 3CO$$

$$\downarrow(-CO)$$

$$[Cl_3MCl_3MCl_3]^{(n+1)-} \qquad \text{--------[2]}$$

The reactions for M = Mo, (n = 1 and 2) were carried out in dichloromethane and, after the vigorous evolution of carbon monoxide, the addition of $[R_4N]Cl$ gave the complexes $(R_4N)_3[Mo_2Cl_9]$ ($R = {}^nPr$) and $(R_4N)_2[Mo_2Cl_9]$ ($R = {}^nBu$) respectively, in high yield. The success of this reaction does not on its own prove the validity of the reaction scheme since a similar reaction designed to produce $[W_2Cl_9]^{3-}$, (ie. $WCl_6 + [W(CO)_5Cl]^- + 2Cl^-$) gave instead a mixture of $[WCl_6]^{2-}$ and/or $W(CO)_4Cl_2$ and $[W(CO)_4Cl_3]^-$. It was suggested that this is probably due to the reduction potential to M (III) being greater for tungsten than for molybdenum.

In 1974, the same group of workers reported[19] another designed route to the $[Mo_2X_9]^{3-}$ anions ($X = Cl^-, Br^-$). Thus, the reaction of $MoCl_5$ with $[Mo(CO)_5Cl]^-$ and $[{}^nBu_4N]Cl$ in dichloromethane gives the compound $({}^nBu_4N)_3[Mo_2Cl_9]$ in 83% yield. The complex $({}^nPr_4N)_3[Mo_2Br_9]$ was isolated from a similar reaction between $MoBr_4$ and $({}^nBu_4N)[MoCO_5Br]$; isolation of the ${}^nBu_4N^+$ salt proved impossible but the addition of $[{}^nPr_4N]Br$ gave the desired product.

The anions $[Mo_2X_8H]^{3-}$ ($X = Cl^-, Br^-$)[20,21] were prepared by the reaction of $Mo_2(CH_3CO_2)_4$ with concentrated HX and precipitated as the caesium or rubidium salts by the addition of $M'X$ ($M' = Cs^+$ or Rb^+). At first,[20] the caesium salt was erroneously assigned the formula $Cs_3[Mo_2Cl_8]$ and an X-ray analysis carried out on this assumption showed the structure of the anion to be similar to that of $[Mo_2Cl_9]^{3-}$ but with one of the bridge positions vacant. Later, however, the hydride ligand was shown to be present, first by chemical methods[22] and then by a recent reinvestigation[23] of the crystal structure of $(C_5H_5NH)_3[Mo_2Cl_8H]$. Thus, the overall reaction can be written (eqn. 3).

$$Mo_2(CH_3CO_2)_4 + 5HX + 3M^{+} + 3X^{-} \rightarrow M'_3[Mo_2X_8H] + 4CH_3CO_2H \quad ---[3]$$

and is thought to proceed in two stages: -

$$Mo_2(CH_3CO_2)_4 + 4HX + 3X^{-} \longrightarrow [Mo_2X_7]^{3-} + 4CH_3CO_2H \quad ------- \quad [3a]$$

$$[Mo_2X_7]^{3-} + HX \longrightarrow [Mo_2X_8H]^{3-} \quad ----- \quad [3b]$$

The second step [3b] can be regarded as an oxidative addition of HX to the binuclear species $[Mo_2X_7]^{3-}$ and this intermediate (for X = Br^{-}) has been isolated as its caesium salt;[24] however, no structural details have yet been reported.

Tungsten: The tungsten compounds $M'_3[W_2Cl_9]$ ($M' = K^{+}$, Et_4N^{+}, Me_4N^{+}) were the first complexes of the type $M'_n[M_2X_9]$ reported in the literature. It was synthesised by Olsson and co-workers[25] in 1914 by the reduction of tungstic acid by tin in conc. HCl, and addition of KCl then precipitated the product as $K_3[W_2Cl_9]$. The other salts $M'_3[W_2Cl_9]$ were made by the addition of M'Cl to a solution of the potassium complex. The bromo complex $K_3[W_2Br_9]$ was produced in 1932 by a similar reaction[26] in conc. HBr. The rubidium salt of the bromo compound has also been synthesised[27] from $K_3[W_2Cl_9]$ by reaction with conc. HBr followed by addition of RbBr. Later, an electrochemical synthesis was devised[28] and further modified[29] to give a better yield (60%) of $K_3[W_2Cl_9]$. This reaction involves the reduction of $WO_3.H_2O$ in a mixture of K_2CO_3 and conc. HCl. The X-ray structure of $K_3[W_2Cl_9]$ has been determined[30] and establishes the confacial bioctahedral configuration.

The dianion $[W_2Cl_9]^{2-}$ can be produced by the oxidation of $[W_2Cl_9]^{3-}$ with iodine,[31] and has been isolated as its $(^nBu)_4N^{+}$ salt. The complex $(^nPr_4N)_2[W_2Br_9]$ has recently been synthesised[32] in 80-90% yield by the oxidative bromination of $^nPr_4N[W(CO)_5Br]$ with 1,2-dibromoethane in refluxing chlorobenzene and shown by X-ray

analysis to have the triply bridged structure,

Titanium (III):- There are two reported syntheses[8] of the anion $[Ti_2Cl_9]^{3-}$ involving either reaction of stoichiometric quantities of $TiCl_3$ and $[R_4N]Cl$ ($R = {}^nBu$) or reduction of $TiCl_4$.

Hetero-metallo complex anions $[MM'X_9]^{3-}$:- As an extension of Wentworth et al's designed syntheses of $[Mo_2X_9]^{n-}$ ($X = Cl^-, Br^-$; $n = 2,3$), attempts were made to synthesise mixed metal complexes.[8,33] For example, from the reaction of $[MoCl_6]^{2-}$ with $CrCl_2$ and Cl^-,* the complex $({}^nBu_4N)_3[CrMoCl_9]$ was isolated and characterised. However, when $[TiCl_6]^{2-}$, $CrCl_2$ and Cl^-* were reacted, an equilibrium mixture of $[Ti_2Cl_9]^{3-}$, $[Cr_2Cl_9]^{3-}$ and $[CrTiCl_9]^{3-}$ was produced and with $[WCl_6]^{2-}$ no $[CrWCl_9]^{3-}$ was formed. The reason for the absence of a reaction with $[WCl_6]^{2-}$ would again appear to be due to the relative ease of reduction to the M (III) species and this is supported by the observation[8] that the $[MoCl_6]^{2-}$ ion is reduced to $[Mo_2Cl_9]^{3-}$ by tin, whereas no reaction occurs with $[WCl_6]^{2-}$.

An equimolar mixture of $[Cr_2Cl_9]^{3-}$ and $[Ti_2Cl_9]^{3-}$ rapidly leads to the same distribution of complexes as was obtained in the reaction of $[TiCl_6]^{2-}$ with $CrCl_2$ and Cl^- (eqn. [4]).

$$[Ti_2Cl_9]^{3-} + [Cr_2Cl_9]^{3-} \rightleftharpoons 2[TiCrCl_9]^{3-} \quad \text{----------} \quad [4]$$

This behaviour can be attributed to the lability of the Ti-Cl bonds of Ti(III)($3d^1$) in $[TiCrCl_9]^{3-}$ unlike the situation in $[CrMoCl_9]^{3-}$ where each metal ion possesses a d^3 configuration (substitutionally inert). This lability is demonstrated by the facile reaction of $[Ti_2Cl_9]^{3-}$ with chloride ion to give $[Ti_2Cl_{10}]^{4-}$ whereas comparable

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*The combination of $CrCl_2$ and Cl^- was employed since it is formally similar to the $[Cr(CO)_4Cl_3]^-$ anion which is unknown.

reactions with $[Cr_2Cl_9]^{3-}$ and $[Mo_2Cl_9]^{3-}$ do not occur.[8]

By analogy with the production of $[Mo_2X_8H]^{3-}$ ions by the reaction[20] of $Mo_2(CH_3CO_2)_4$ with HX at elevated temperatures (60°C), the heterometallo complex $MoW(CH_3CO_2)_4$ reacts even at 0°C to give the $[MoWX_8H]^{3-}$ ion.[34] This difference demonstrates the greater reactivity of the metal-metal bond in heteronuclear derivatives towards oxidative addition.

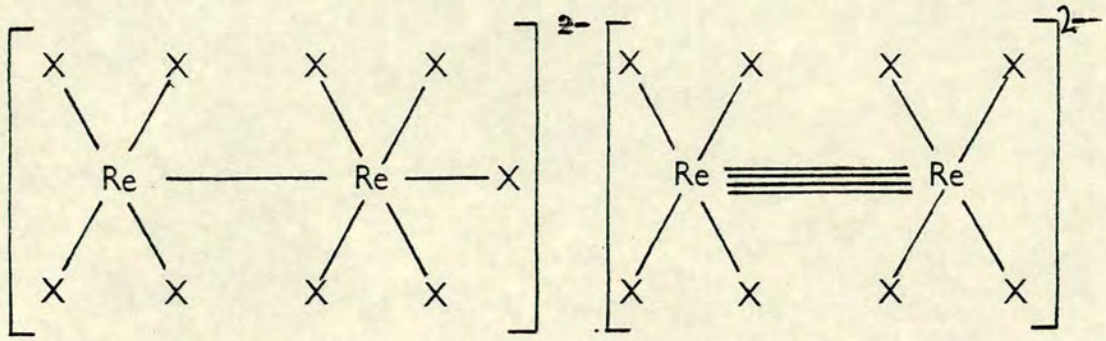
Group VII: Manganese, Technetium and Rhenium

Brief reports have appeared in the literature on the following compounds of rhenium. $(^nBu_4N)[Re_2Cl_9]$[35,36], $(Ph_4As)[Re_2Cl_9]$[35], $(^nBu_4N)[Re_2Br_9]$[35], $(^nBu_4N)_2[Re_2X_9]$ ($X = Cl^-$, Br^-)[35]; $(Ph_4As)_2[Re_2Cl_9]$[37,38] and $(Et_4N)_2[Re_2Cl_9]$[38]. The complexes $(^nBu_4N)[Re_2X_9]$ have been made by the reaction of $(^nBu_4N)_2[Re_2X_8]$ with chlorine or bromine gas in dichloromethane[35] and an X-ray analysis (when $X = Cl^-$) confirms the triply bridged configuration of the anions.[39]

The dianions can be prepared by a number of synthetic routes. The complex $(Ph_4As)_2[Re_2Cl_9]$ was first prepared[37] by the reaction of $ReCl_4$ with HCl in methanol followed by the addition of Ph_4AsCl, and the $^nBu_4N^+$ salts were synthesised later from $(^nBu_4N)[Re_2X_9]$ by oxidation with copper ($X = Cl^-$) and iron ($X = Br^-$) in acetone.[35]

The reaction of $ReCl_5$ with $[Ph_4As]Cl.HCl$ or $[Et_4N]Cl.HCl$ in an acetone/water/chloroform (30:1:15) mixture gives the $[Re_2Cl_9]^{2-}$ ion in good yields.[38] These dianions may have a different structure (6) from that of the $[Re_2X_9]^-$ anions, and be based on the structure of $[Re_2X_8]^=$ (7)

The X-ray analyses of these compounds (6) were reported as being carried out;[35] however, no mention of this can be found in the later literature.



(6) (7)

Recently, the reactions of the compound $(^{n}Bu_4N)\left[Re_2Cl_9\right]$ with tertiary phosphines have been investigated.[40] Thus, the reaction with PPh_3 in a methanol/HCl solution gave the complex $Re_2Cl_6(PPh_3)_2$. When more basic phosphines were used, further reduction occurred and with $PEtPh_2$, the product was $Re_2Cl_5(PEtPh_2)_3$ and with PEt_3, it was $Re_2Cl_4(PEt_3)_4$. The latter is claimed to be the first four electron reduction of a metal-metal bonded binuclear complex in which the metal-metal bond is retained.

Group VIII: No complexes of the type $\left[M_2X_9\right]^{n-}$ are yet known for M = Co, Ni, Os, Ir, Pd or Pt.

Iron: The compound $(C_5H_5NH)_3\left[Fe_2Cl_9\right]$ was first reported[41] in 1922 and again in 1961.[14] It was made by the reaction of iron(III)chloride with pyridine in conc. HCl. No further mention of this anion has since appeared in the literature.

Ruthenium: A brief report[42] on the synthesis of $\left[(C_8H_7)_4N\right]\left[Ru_2Cl_9\right]$ appeared in 1977 and it was made by shaking $K_2\left[Ru(H_2O)Cl_5\right]$ in water with $\left[(C_8H_{17})_4N\right]Cl$ in dichloromethane. The analogous bromo compounds $M'_3\left[Ru_2Br_9\right]$ ($M' = K^+$, Rb^+, Cs^+) dominate Ru(III) bromo chemistry[43] and they have been isolated from many different reactions initially designed to prepare other bromo complexes. For example, reaction of $RuBr_3$ and KBr in conc. HBr gives black crystals of $K_3\left[Ru_2Br_9\right]$. The rubidium and caesium salts can also be isolated by careful addition

of the appropiate bromide.

Rhodium: The first reported synthesis[44a] of a $[Rh_2X_9]^{3-}$ anion was that of $(Et_4N)_3[Rh_2Cl_9]$ in 1927. $RhCl_3$ was reacted with conc. HCl followed by addition of $[Et_4N]Cl$ to precipitate the complex. Ferguson and co-workers later extended this[44b] to the syntheses of the alkali metal salts and the bromo complexes by the following preparative routes (Figs. 1.1 and 1.2).

Fig 1.1

Preparative routes to the $[Rh_2Cl_9]^{3-}$ anion

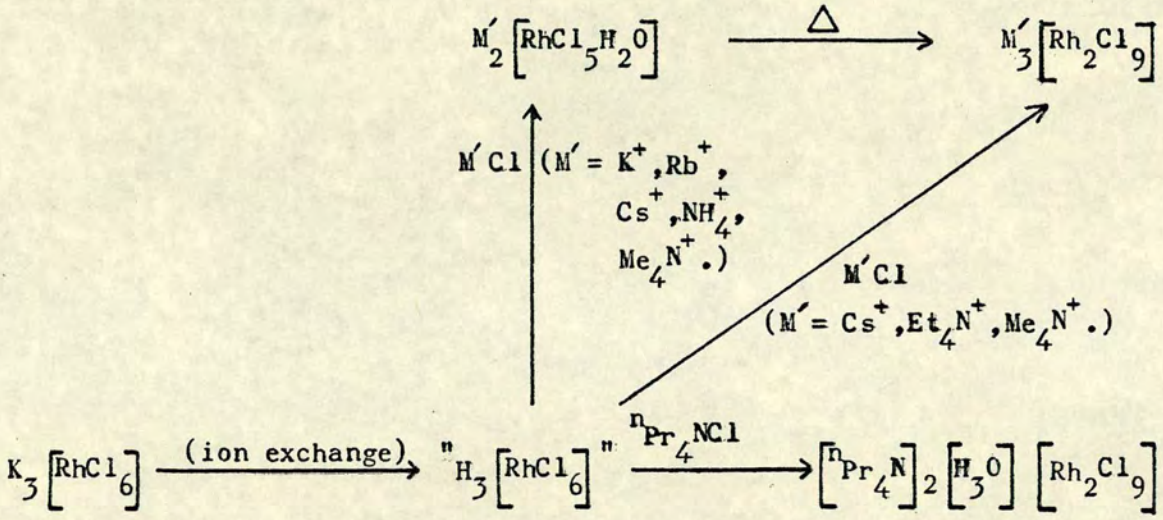
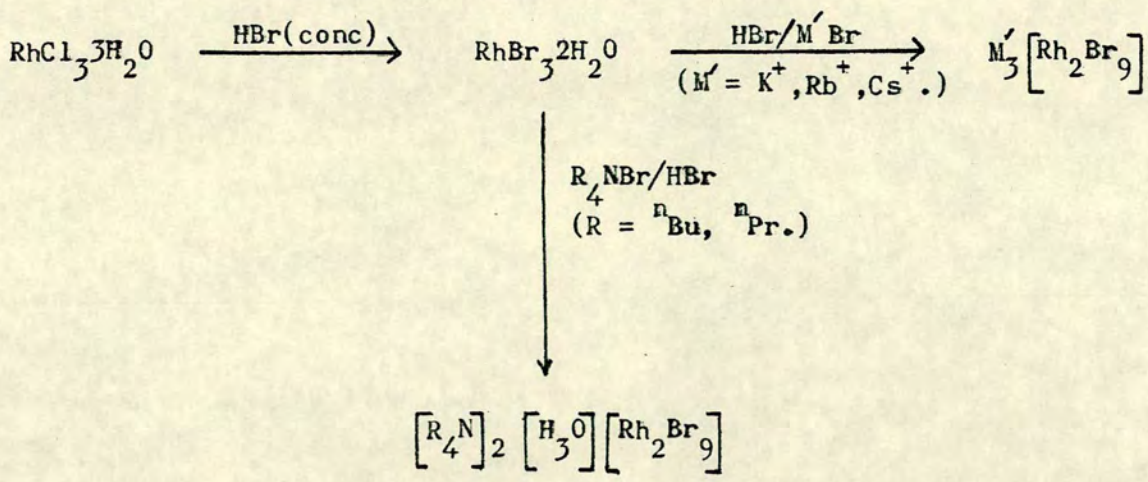


Fig 1.2

Preparative routes to the $[Rh_2Br_9]^{3-}$ anion



1.3 Discussion of the bonding as related to the reactivity of the complexes $M'_3[M_2X_9]$.

The reactions of the anions $[M_2X_9]^{3-}$ (M = Cr, Mo, W) are consistent with the strength of the metal-metal interaction in these complexes. Thus, when M = Cr, where there is a long M-M distance of 312 p.m.[13] and magnetic measurements (μeff = 3.76)[9] indicate little M-M interaction, the reaction with pyridine[9] proceeds at ambient temperature with bridge cleavage to give mer-$CrCl_3(py)_3$. However, when M = W, where the M-M distance is significantly shorter (240.9 p.m.)[30] and μeff* = 0.43,[9] indicating a strong M-M interaction, the reaction with pyridine[29] gives the complex $W_2Cl_6(py)_4$ retaining the binuclear unit. The behaviour of the molybdenum anion is intermediate between these two extremes as would be expected from the experimental data ie. d(M-M) = 265.5 pm.[10] and μeff* = 0.60[17] and the reaction with pyridine at 200°C gives mer-$MoCl_3(py)_3$. The anion $[Mo_2Cl_8H]^{3-}$ where d(M-M) = 238 pm.[23] reacts at 200°C to give the dimeric complex $Mo_2Cl_4(py)_4$ which then reacts further with pyridine[45] to give mer-$MoCl_3(py)_3$. The bromo anion $[Mo_2Br_8H]^{3-}$, where d(M-M) = 243.9 pm.[23] reacts similarly but much faster. Although these observations are consistent with the relative strengths of the metal-metal interactions, they may also be due to kinetic factors which have not been investigated as yet.

1.4 Triply bridged binuclear complexes containing π-bonded carbocyclic ligands.

The first report of a compound containing both a triple bridge and a π-bonded carbocyclic ligand was by Kang and Maitlis,[46] who isolated the triple chloro and hydroxo bridged η^5-pentamethylcyclopentadienyl rhodium (III) complexes (8a) and (8b).

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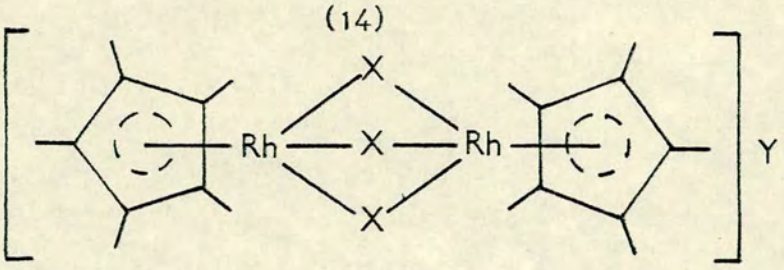
* μeff per metal ion.

(14)



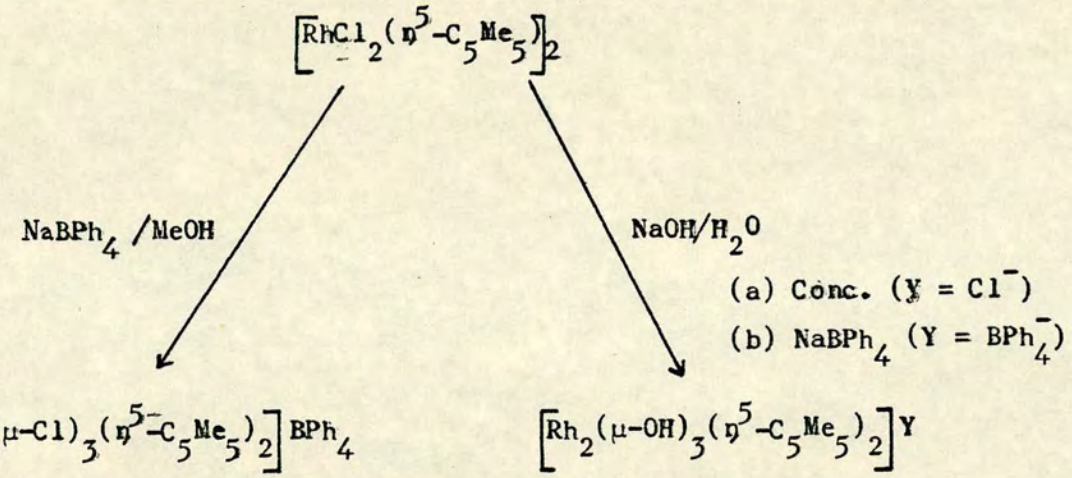
(8a), X = Cl^-; Y = BPh_4^-.

(8b), X = OH^-; Y = Cl^-, BPh_4^-.

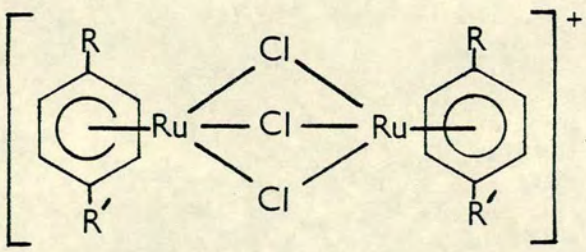
These were prepared from the dimeric compound $\left[RhCl_2(\eta^5\text{-}C_5Me_5)\right]_2$ as shown in Fig. 1.3.

Fig. 1.3.

Syntheses of triple bridged complexes of $\eta^5\text{-}C_5Me_5\text{-}Rh(III)$.



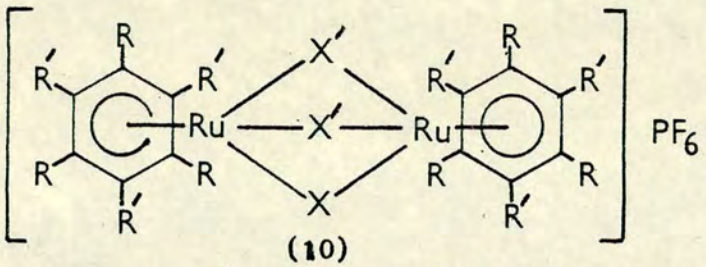
In 1974, Bennett and Smith[47] isolated the isoelectronic ruthenium(II) cations (9a) and (9b), by first refluxing the dimer $\left[RuCl_2(\eta^6\text{-arene})\right]_2$ in water to give an orange solution and then adding NH_4PF_6.



(9a), R = R′ = H

(9b), R = Me, R′ = $CH(Me)_2$

Very recently, the same group briefly reported the synthesis of the analogous hydride bridged compounds, (10), which were found to be very active catalysts for the hydrogenation of arenes to cyclohexanes.[48]



(10)

(R = R′ = Me ; X = Cl^-, X′ = H^-).
(R = Me, R′ = H ; X = Cl^-, X′ = H^-).
(R = Me, R′ = H ; X = X′ = H^-).

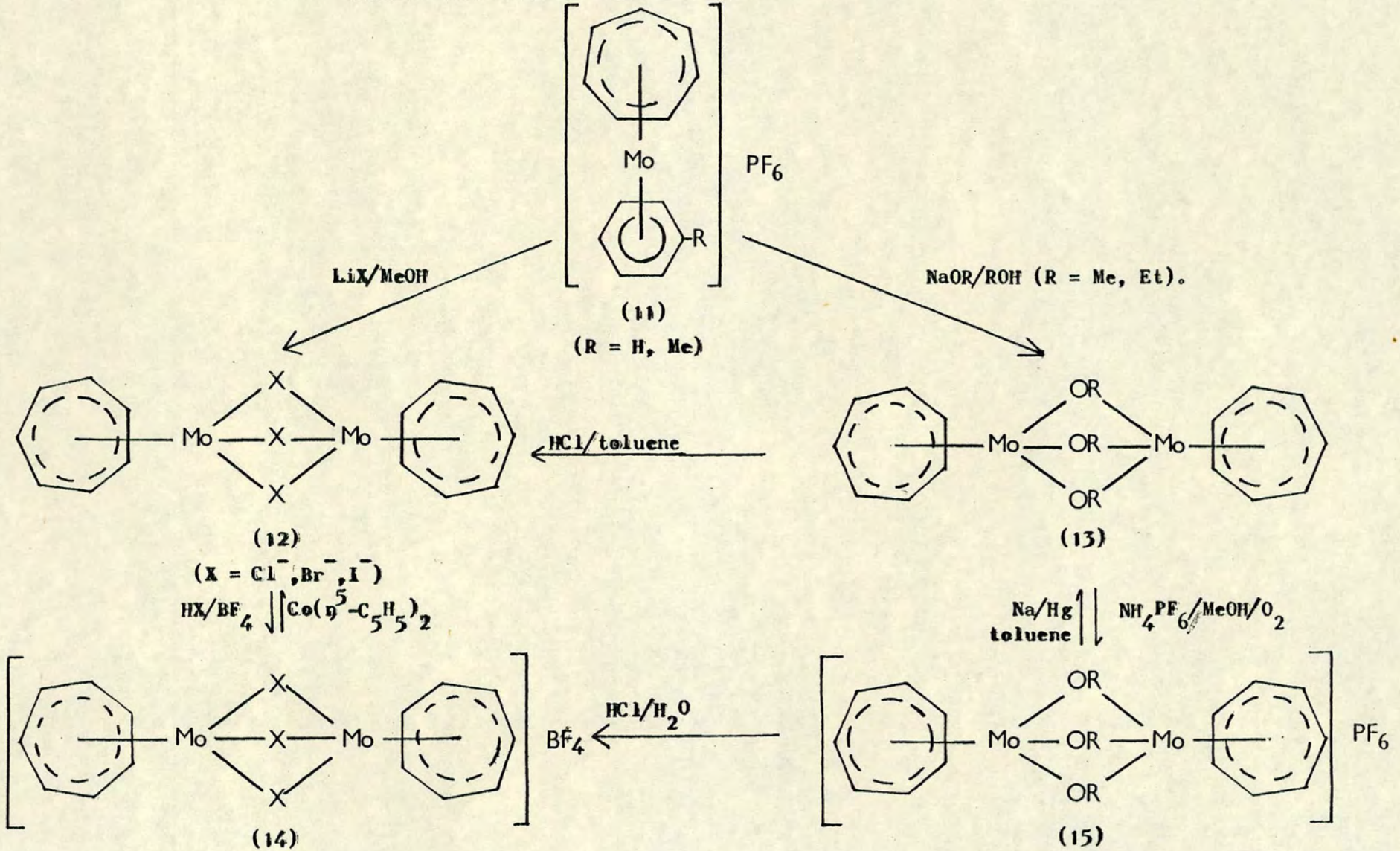
These complexes were prepared by the reaction of the dimers $[RuCl_2(\eta^6\text{-}C_6R_3R'_3)]_2$ in propan-2-ol at elevated temperatures (80°C). Further studies on triple bridged halide, hydroxo and alkoxo complexes of ruthenium (and osmium) containing π-arene ligands are described in Chapters 2 and 3.

A large number of triple bridged molybdenum complexes have recently been synthesised.[49-54] These include the symmetric species $[Mo_2(\mu\text{-}X)_3(\eta^7\text{-}C_7H_7)_2]^n(Y)_n$ (n = 0, X = Cl^-, Br^-, I^-, OR^- (R = Me, Et, Ph, p-Me-C_6H_4, p-Cl-C_6H_4); n = 1, X = Cl^-, Br^-, I^-, OR^- (R = Me, Et), Y = $[MoCl(C_2(CF_3)_2)_3]^-$; n = 1, X = Cl^-, Br^-, I^-, OR^- (R = Me, Et), Y = PF_6^- and the mixed bridged compounds $Mo_2(\mu\text{-}X)_2(\mu\text{-}X')(\eta^7\text{-}C_7H_7)_2$, X = Cl^-, Br^-, I^-, SCN^-; X′ = Cl^-, Br^-.

The first report of this type of compound appeared in 1974 when the mixed sandwich complex (11) was treated with alcohols, sodium alkoxides and lithium halides respectively[52] (see Fig. 1.4.).

Fig 1.4

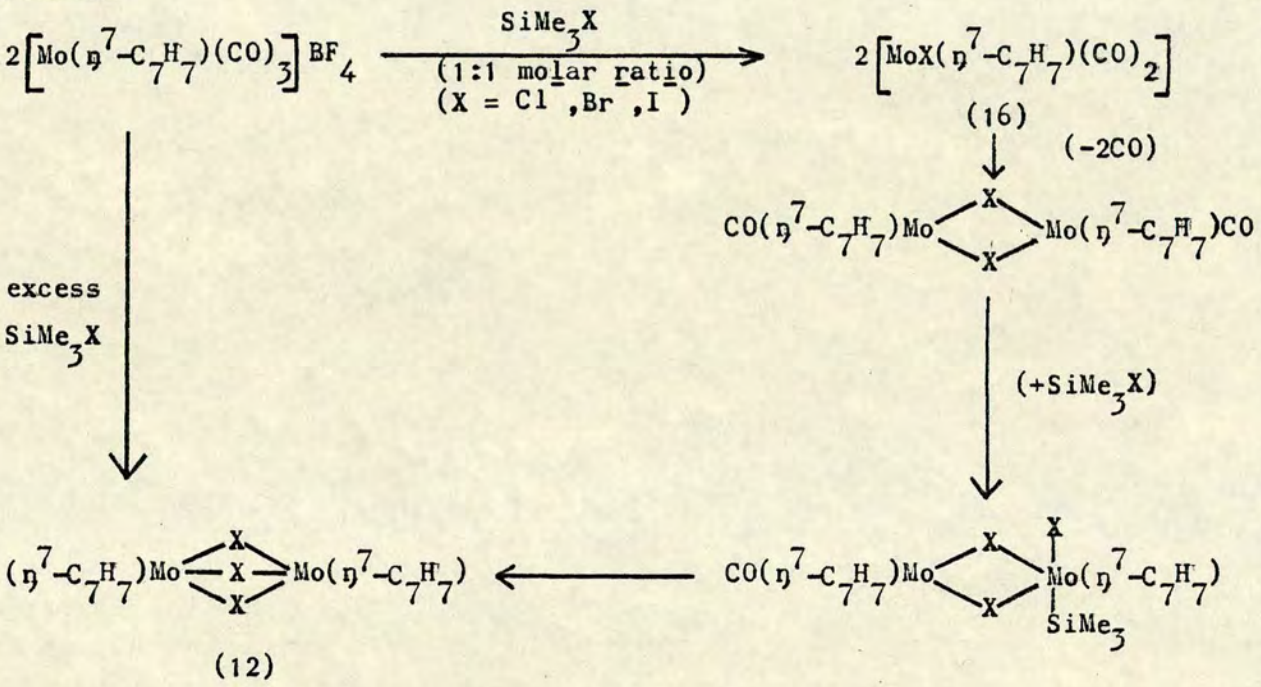
Reactions of $[Mo(\eta^6\text{-}C_6H_5R)(\eta^7\text{-}C_7H_7)]PF_6$



An alternative route to the neutral, halo bridged complexes (12) involving the reaction of $[Mo(\eta^7\text{-}C_7H_7)(CO)_3]BF_4$ with $SiMe_3X$ has been reported [49,51] (see Fig. 1.5).

Fig. 1.5.

Postulated mechanism for the reactions of $[Mo(\eta^7\text{-}C_7H_7)(CO)_3]BF_4$ with $SiMe_3X$.



Since the complexes (16) ($X = Cl^-$, Br^-, I^-) can be isolated the possibility of synthesising mixed bridge compounds by reaction with $SiMe_3X'$ is obvious. Thus, when $X = Br^-$ and $X' = Cl^-$, the product $Mo_2(\mu\text{-}Cl)(\mu\text{-}Br)_2(\eta^7\text{-}C_7H_7)_2$ has been isolated and characterised as a true mixed bridge complex; however, when $X = Cl^-$ and $X' = Br^-$, there is evidence for the presence of some $Mo_2(\mu\text{-}Cl)_3(\eta^7\text{-}C_7H_7)_2$ in the product.[51] The binuclear complexes (12) are readily oxidised to the cationic complexes (14) (see Fig. 1.4), and indeed the reaction with the mild oxidising reagents $[p\text{-}NO_2C_6H_4N_2]BF_4$ or $[PhN_2]PF_6$ gave these cations as the BF_4^- and PF_6^- complexes respectively.[49,51] The reaction of $[Mo(\eta^7\text{-}C_7H_7)(CO)_3]BF_4$ with iodine gave the complex $[Mo_2(\mu\text{-}I)_3(\eta^7\text{-}C_7H_7)_2]I_3$.[49] One other reaction leading to the cationic compounds (14) (X = Cl ,Br)

has been reported, namely the reaction of $MoX(\eta^7\text{-}C_7H_7)(CO)_2$ with $C_2(CF_3)_2$ which gives $\left[Mo_2(\mu\text{-}X)_3(\eta^7\text{-}C_7H_7)_2\right]\left[MoX(C_2(CF_3)_2)_3\right]$ whose structure (for $X = Cl^-$) was determined by X-ray crystallography.[54]

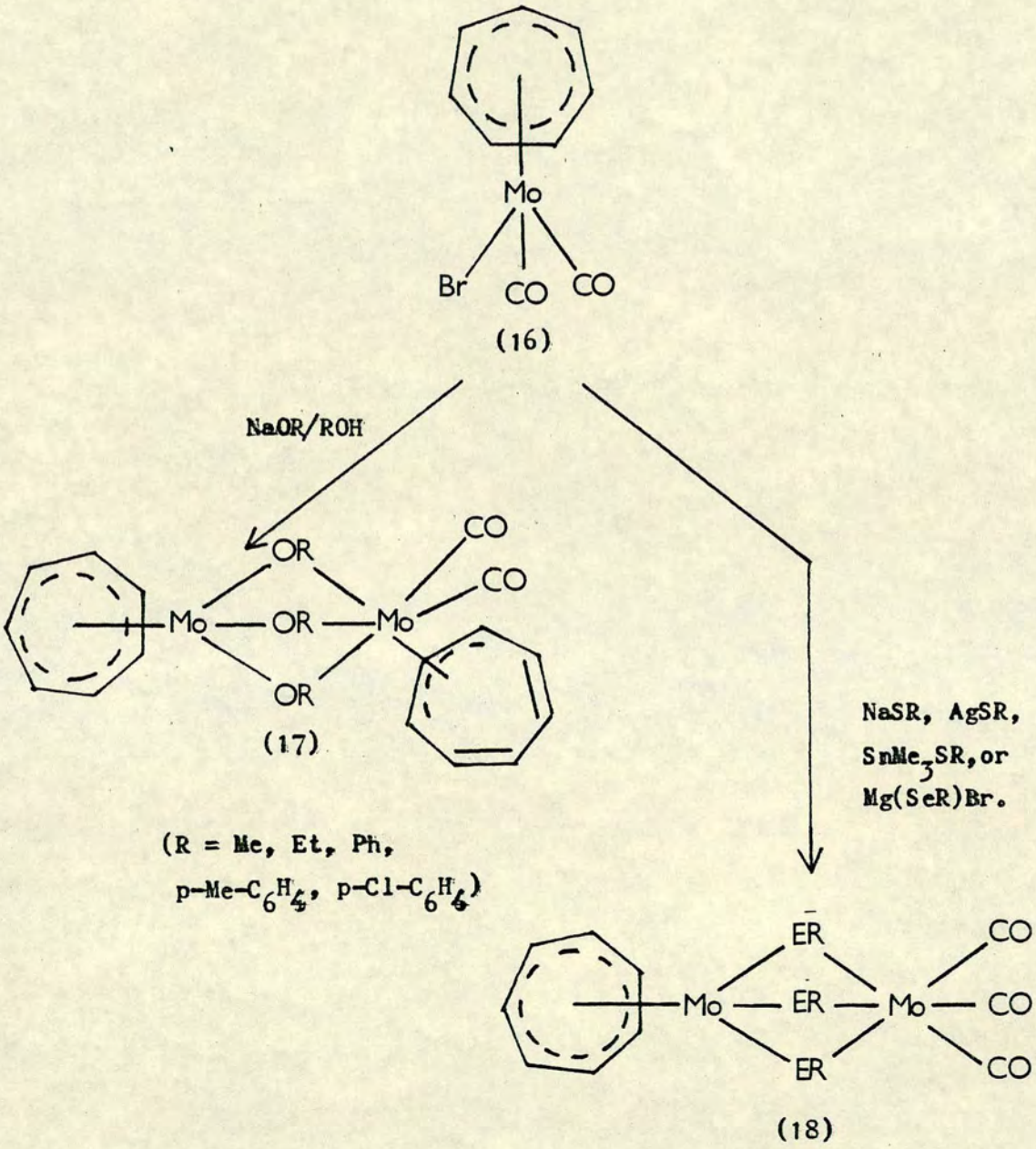
The neutral complexes (12) and (13) are paramagnetic having one unpaired electron per molecule, and they are formulated as mixed valence compounds. However, although e.s.r. studies show that the odd electron is associated with both molybdenum atoms, [53] ESCA studies[50] on the complexes (12) indicate two distinct oxidation states for the molybdenum atoms. The cationic complexes (14) and (15) are diamagnetic and are formulated as binuclear Mo(I)/Mo(I) compounds with a strong M-M interaction, and indeed, the X-ray structure of $\left[Mo_2(\mu\text{-}Cl)_3(\eta^7\text{-}C_7H_7)_2\right]\left[MoX(C_2(CF_3)_2)_3\right]$ confirms this since d(Mo-Mo) = 306 p.m.[54] lies within the range expected for a Mo-Mo bond.[55]

The unsymmetrical complexes (17), (R = Me, Et, Ph, p-Me-C_6H_4, p-Cl-C_6H_4) and (18) (see Fig. 1.6.) (E = S, R = Me, Et, ^{n}Pr, ^{n}Bu, ^{t}Bu; E = Se, R = Ph, ^{n}Bu, ^{t}Bu) are also known.[57] Thus, reaction of the compound (16) ($X = Br^-$) with alkoxides and phenoxides,[56] generate the paramagnetic compounds (17), whereas the corresponding reactions with thiols and selenols[57] gave the diamagnetic compounds (18) (see Fig. 1.6.). A crystal structure determination[56] on (17) (R = Me) confirms the triple bridged formulation, and e.s.r. measurements indicated that the unpaired electron was situated exclusively on the Mo atom bonded to the $\eta^7\text{-}C_7H_7$ ring.

An X-ray analysis[57] on (18) (E = S, R = Me) confirms the triple bridged configuration.

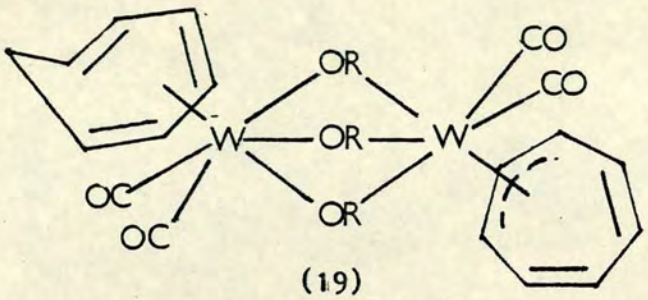
Fig. 1.6.

Syntheses of $Mo_2(\mu\text{-}OR)_3(\eta^7\text{-}C_7H_7)(\eta^3\text{-}C_7H_7)(CO)_2$ (17) and $Mo_2(\mu\text{-}ER)_3(\eta^7\text{-}C_7H_7)(CO)_3$ (18).



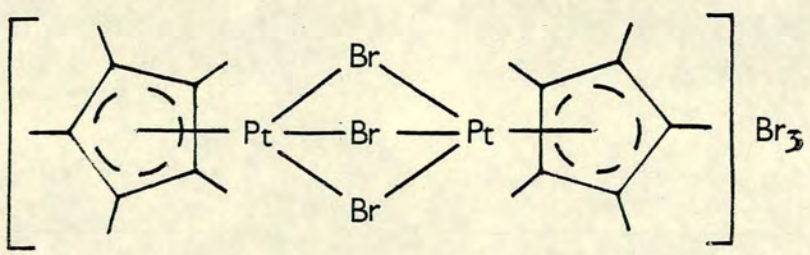
The corresponding reaction with Mg(TeR)Br (R = Ph) gives the double bridged dimer $Mo_2(\mu\text{-}TeR)_2(\eta^7\text{-}C_7H_7)_2(CO)_2$. The formation of the double bridged complex is thought to be due to the larger steric requirements of the tellurium atom preventing the formation of a triple bridge.

The reaction of the tungsten analogue of (16), namely $WI(\eta^7\text{-}C_7H_7)(CO)_2$ with alkoxides[58] does not give the tungsten analogue of (17); instead, the reduction of one $\eta^7\text{-}C_7H_7$ ligand occurs, and the diamagnetic complexes (19) (R = Me, Et, ^{n}Pr, Ph) are formed.



(19)

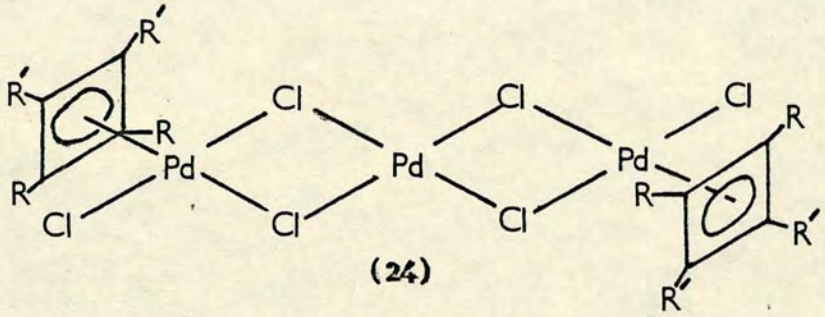
A wide variety of chemistry[59] has been developed for the $\eta^5\text{-}C_5Me_5$ complexes of rhodium (III) and iridium (III), and to ascertain whether the inertness of the metal to $\eta^5\text{-}C_5Me_5$ bonding was a general feature, attempts to synthesise other group VIII complexes of this ligand have been made. The reaction of $PtCl_2(\eta^4\text{-}C_5Me_5H)$ with bromine[60] gave a complex which was characterised as the triple bridged compound (20), Reactions of complex (20) with $Ag[PF_6]$ in co-ordinating solvents resulted in the formation of unstable adducts, in contrast to the analogous Rh (III) and Ir(III) compounds which give complexes of the type $[M(\eta^5\text{-}C_5Me_5)L_3](PF_6)_2$ (M = Rh, Ir; L = MeCN, acetone, d.m.s.o.etc.). Thus, the reactivity of the M-$\eta^5\text{-}C_5Me_5$ bond is dependent on the nature of M.



(20)

A brief report on triple bridged cyclobutadiene complexes of palladium (II) has appeared in the literature.[61b] The reactions of $PdCl_2(PhCN)_2$ with $^tBuC \equiv CMe$ were investigated and the complexes (21), (22) and (23) isolated.(see Fig. 1.7.).

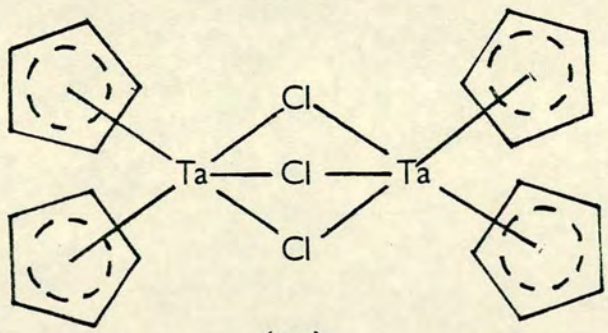
Other cyclobutadiene complexes analogous to (22) have been reported[62,63,64,65] and were originally formulated as having the configuration(24).



(24)

However, their ir. spectra were inconsistent with this structure and the X-ray analysis[61b] of (22a) ($Y = \frac{1}{2}Pd_2Cl_6$) confirms the triple bridged nature of the cation.

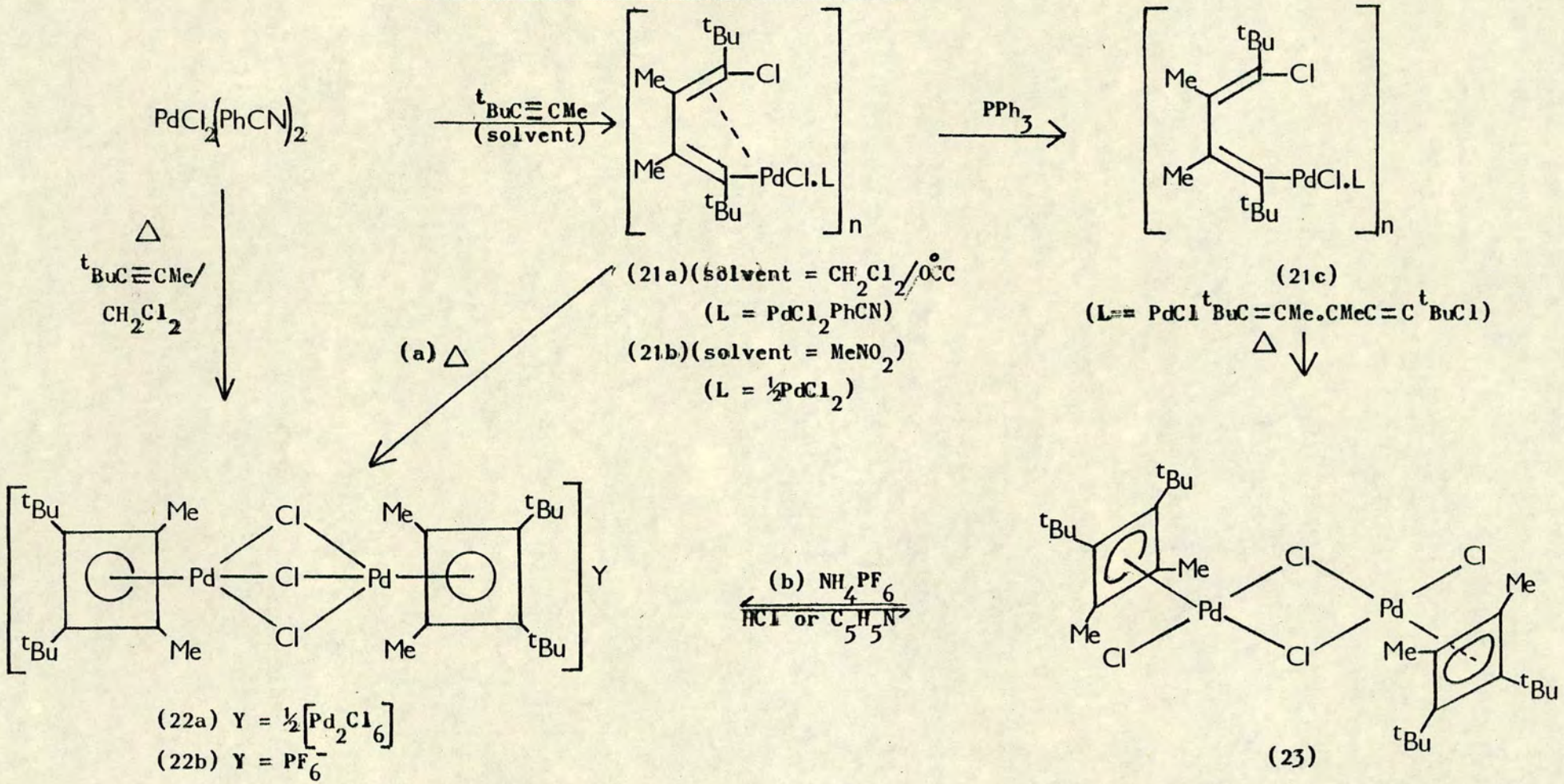
Finally, a triple bridged tantalum complex (25) has been briefly mentioned in the literature.[66] The reaction of $LiPPh_2$ with $TaCl_5$ and NaC_5H_5 gave, after removal of P_2Ph_4 by sublimation at 60°C, a purple solid at 120°C which was identified as (25). The compound (25) was formulated as a mixed valence complex of Ta(III) and Ta(IV) with one unpaired electron per molecule.



(25)

Fig 1.7

Reactions of $PdCl_2(PhCN)_2$ with $^tBuC{\equiv}CMe$



(22)

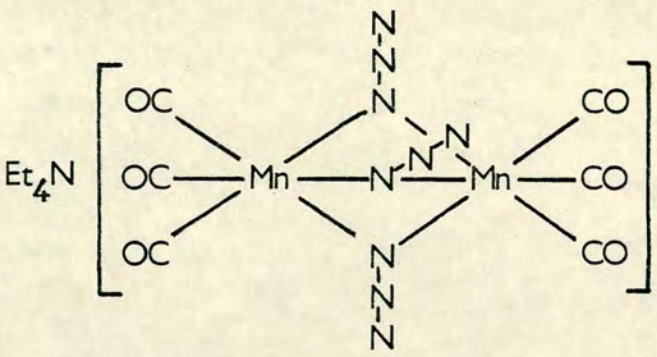
1.5 Compounds of the type $\left[M_2(\mu\text{-}X)_3X_nL_{(6-n)}\right]^z$

There are many compounds of the general formula $\left[M_2(\mu\text{-}X)_3X_nL_{(6-n)}\right]^z$, (M = transition metal; X = halide; L = a two electron donor ligand eg. CO, CS tertiary phosphines), and of particular interest in our laboratories are the compounds where M = Ru, Os; L = PR_3, AsR_3. Therefore, it is appropropriate to discuss these and analogous complexes of other transition metals at this point. Further studies on these types of complex are described in Chapter 4.

1.6 The compounds $\left[M_2(\mu\text{-}X)_3(CO)_6\right]^z$ and related derivatives.

Complexes of this type are known for the transition metals manganese, rhenium, chromium, molybdenum and tungsten.

Manganese and Rhenium: The first report of a triple bridged binuclear hexacarbonyl of manganese appeared in 1971 when the triple azido bridged compound (26) was isolated.[67] Complex (26) was prepared by the reaction of NaN_3 with $MnBr(CO)_5$ in H_2O/ethanol, followed by addition of $\left[Et_4N\right]Cl$. The same reaction carried out in refluxing thf gave the mixed bridged complexes $Et_4N\left[Mn_2(\mu\text{-}N_3)_n(\mu\text{-}NCO)_{3-n}(CO)_6\right]$ (n = 0,1,2). These compounds were also obtained from complex (26) by reaction with CO and the compound (n = 0) can be prepared directly from $MnBr(CO)_5$ by reaction with KNCO. X-ray analysis[67] of (26) shows that the N_3^- groups are bonded through only one nitrogen.

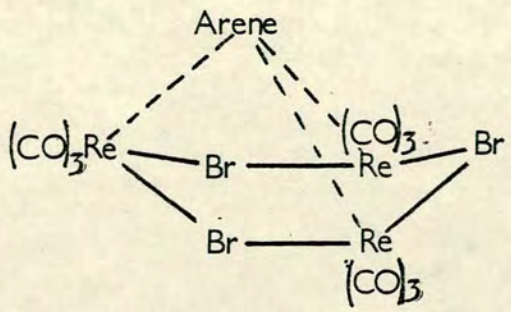


(26)

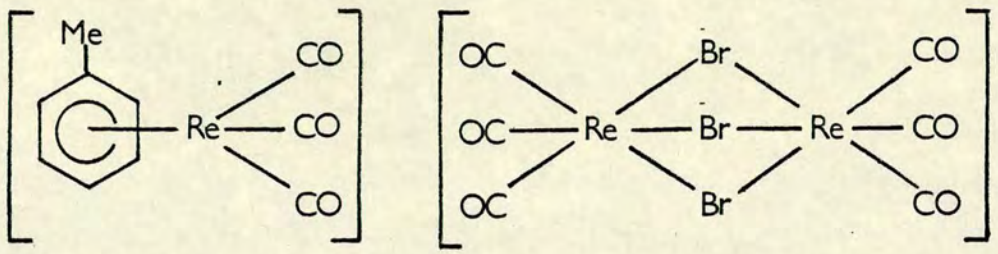
The mixed bridged complexes undergo bridge cleavage with PPh_3 to give a mixture of the compounds $Mn(NCO)(PPh_3)_2(CO)_3$ and $MnN_3(PPh_3)_2(CO)_3$, which have been obtained pure by the reaction of $MnCl(PPh_3)_2(CO)_3$ with NaN_3 and KNCO respectively.[68]

The halo bridged complexes $Et_4N\left[Mn_2(\mu\text{-}X)_3(CO)_6\right]$ ($X = Cl^-$, Br^-) have been obtained in low yield (19%) by the photolysis of $Mn_2(CO)_{10}$ in CHX_3 in the presence of $\left[Et_4N\right]X$;[69a] however, the complex (for $X = Br^-$) could not be obtained in a pure state. A very recent report[69b] gave a better preparative route to these complexes; ($X = Cl^-$, Br^-). Thus, the reaction of $MnX(CO)_5$ with $\left[Et_4N\right]X$ in $CHCl_3$ gave the compounds in high yields (90%). The rhenium compounds $Et_4N\left[Re_2(\mu\text{-}X)_3(CO)_6\right]$; ($X = Cl^-$, Br^-, I^-) were produced similarly.

The anions $\left[Re_2(\mu\text{-}X)_3(CO)_6\right]^-$ ($X = Cl^-$, Br^-) have also been obtained with unusual counterions.[70] Thus, the reaction of $ReX(CO)_5$ with the porphyrins, octaethyl porphyrin (H_2OEP) ($X = Cl^-$) and mesoporphyrin IX dimethyl ester ($H_2MP(IX)DME$) ($X = Br^-$) gave the complexes $A\left[Re_2(\mu\text{-}X)_3(CO)_6\right]$ ($A = H_3OEP^+$ and $H_3MP(IX)DME^+$ respectively). The structure of the complex (for $X = Cl^-$) was determined by X-ray crystallography. The anion $\left[Re_2(\mu\text{-}Br)_3(CO)_6\right]^-$ can also be prepared by the reaction of $Re(CO)_5Br$ or $Re_2Br_2(CO)_8$ with arenes.[71] The complexes isolated from these reactions had the empirical formula $Re_3Br_3(CO)_9$-arene and were originally assigned the structure(27).



X-ray analysis[72] on the complex (arene = toluene) showed the correct formulation to be (28).



(28)

The compound $\left[Re(\eta^6\text{-}C_6Me_6)(CO)_3\right]\left[Re_2(\mu\text{-}Cl)_3(CO)_6\right]$ was also prepared by this route.

The complexes $Et_4N\left[Re_2(\mu\text{-}X)_3(CO)_6\right]$, ($X = H^-$, OEt^-, $OCH(CH_3)_2^-$), have been prepared[73] by the reaction of the dianion $\left[Re_2H_9\right]^{2-}$ with CO in an alkaline, alcoholic media (eqn. [5]).

$$(Et_4N)_2\left[Re_2H_9\right] \xrightarrow[ROH/\left[Et_4N\right]OH]{CO} Et_4N\left[Re_2(\mu\text{-}OR)_3(CO)_6\right] \quad (R = Et, CH(CH_3)_2) \qquad \text{-------[5].}$$

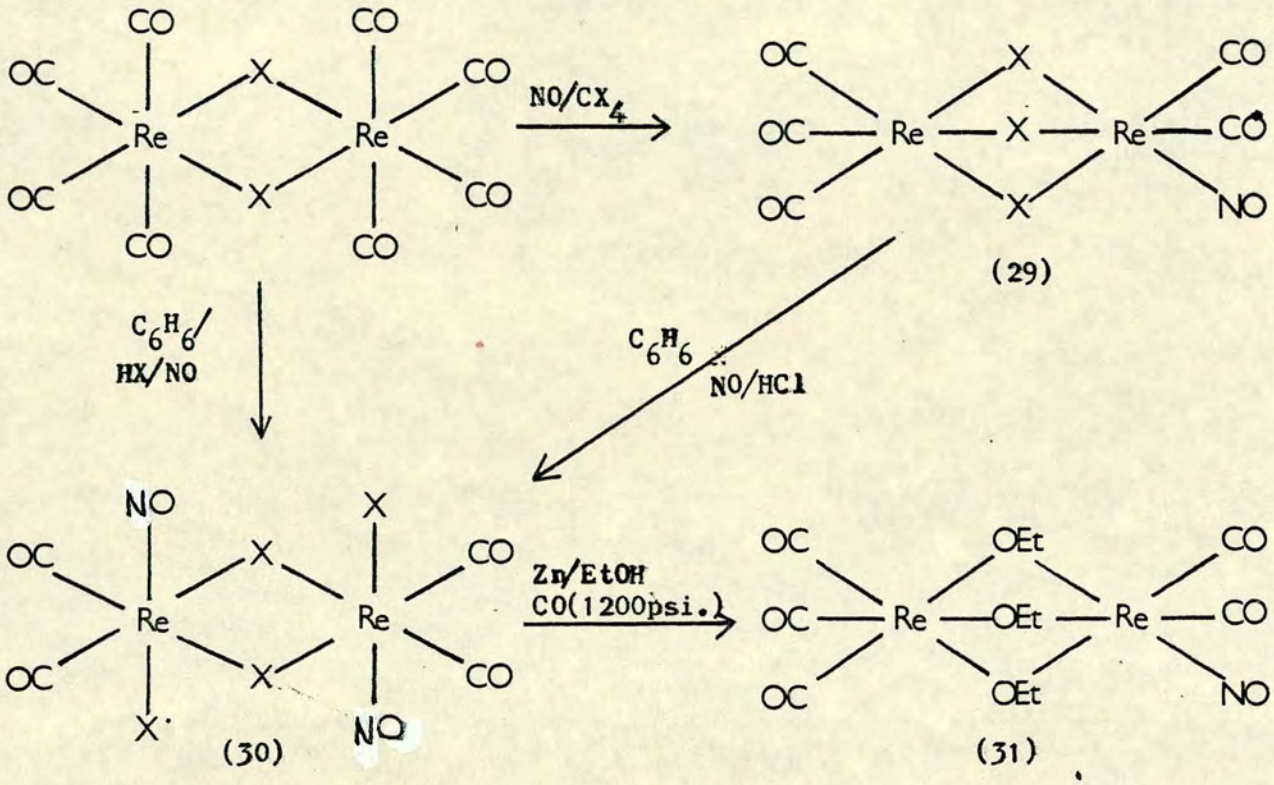
When $R = CH(CH_3)_2$, a red precipitate was also obtained, which was shown to be a mixture of rhenium carbonyl hydrides, from which the compound $Et_4N\left[Re_2(\mu\text{-}H)_3(CO)_6\right]$ could be separated by chromatography.

The reaction of $Re_2Cl_2(CO)_8$ in CCl_4 with NO gave the neutral complex[74] (29) ($X = Cl^-$) and a similar reaction with $Re_2Br_2(CO)_8$ gave a mixture of (29) ($X = Br^-$) and $Re_2X_4(CO)_4(NO)_2$ (30) ($X = Br^-$). The reaction of $Re_2Cl_2(CO)_8$ with NO and HCl in benzene[75] gave the complex (30) ($X = Cl^-$) and reacting the compound (29) ($X = Cl^-$) with NO and HCl also gave (30) ($X = Cl$).[74] Thus, the reaction of $Re_2Cl_2(CO)_8$ with NO and HCl is thought to proceed via the slow formation of (29) ($X = Cl^-$) (see Fig 1.8). The reaction of (30) ($X = Cl^-$) with zinc dust

in ethanol under a pressure of CO gives the triple ethoxo bridged complex (31).[74]

Fig. 1.8.

Reactions of $Re_2X_2(CO)_8$ with NO and HX.

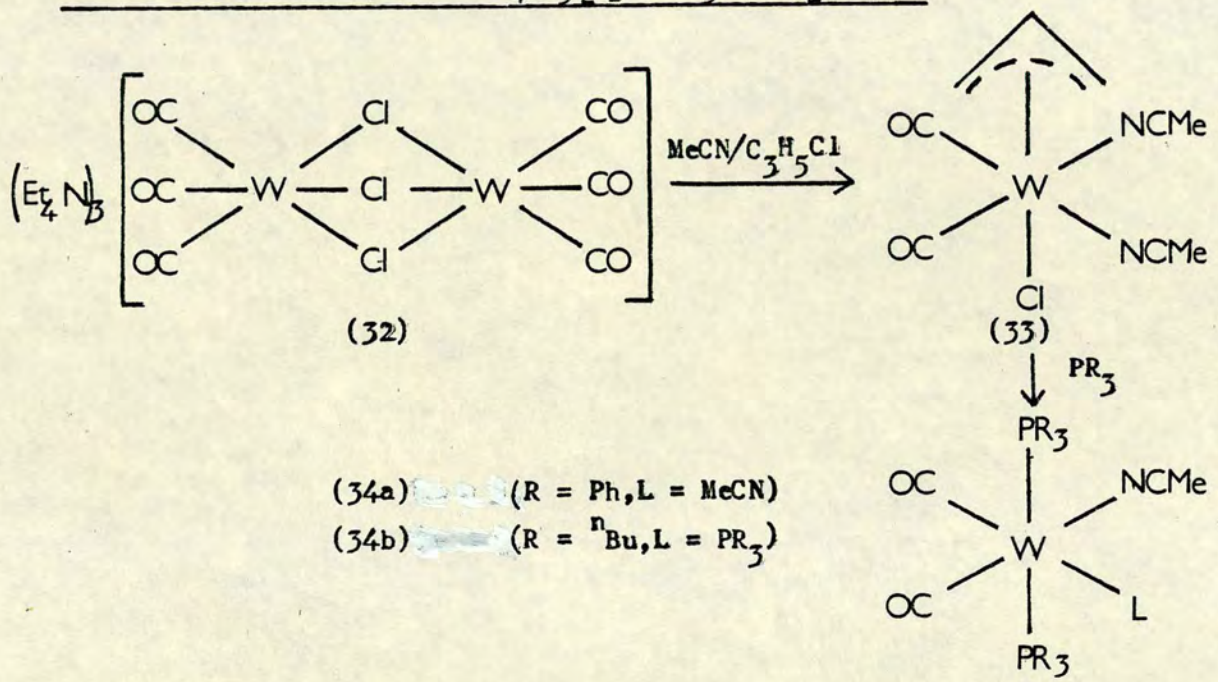


Chromium, Molybdenum and Tungsten: The compounds $M'_3[M_2(\mu\text{-}X)_3(CO)_6]$ ($M' = K^+$; M = Mo, W; $X = OH^-$), were first reported in 1959 when they were prepared by the alkaline hydrolysis of $M(CO)_6$.[76,77] The triple bridge formulation was confirmed in 1970 when the X-ray structure of the complex (M = W) was determined.[78] The analogous complexes ($M' = Et_4N^+$; M = Cr, $X = F^-$, Cl^-, Br^-, I^-, OEt^-, SCN^-, N_3^-; M = Mo, $X = F^-$, Cl^-, Br^-, I^-, OH^-, SCN^-, N_3^-; M = W, $X = F^-$, Cl^-, Br^-, I^-, OH^-, OEt^-.) have also been obtained by the reaction of either $M(\eta^6\text{-arene})(CO)_3$ (arene = toluene or mesitylene) or $M(CO)_6$ with $[Et_4N]X$ in ethanol.[79,80]

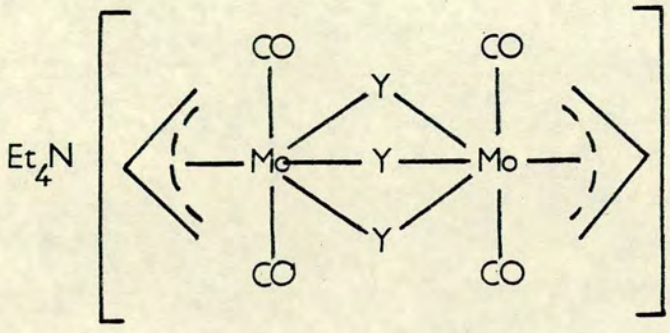
Reaction of the tungsten complex (32) with allyl chloride in acetonitrile gives the monomeric complex $WCl(\eta^3\text{-}C_3H_5)(CO)_2(MeCN)_2$ (33) which reacts with PR_3 (R = Ph, ^nBu) to give the complexes $W(CO)_2(PR_3)_2(MeCN)L$ (34) (R = Ph, L = MeCN; R = ^nBu, L = PR_3)[80] (see Fig. 1.9).

Fig. 1.9.

Reactions of the complex $(Et_4N)_3[W_2(\mu\text{-}Cl_3)(CO)_6]$ (32).



The compound (33) is an example of a seven co-ordinate complex and compounds containing both a triple bridge and an η^3-allyl ligand are known, in which the metal atom is also seven co-ordinate.[81] Thus, the reactions of the compounds $Et_4N[MoX(CO)_5]$ ($X = Cl^-$, Br^-, I^-) with allyl halides (C_3H_5Y) ($Y = Cl^-$, Br^-) in tetrahydrofuran gives the complexes (35) ($Y = Cl^-$, Br^-). The compounds (35) were found to contain only the halide Y^- derived from the allyl compound.



(35)

When allyl iodide or $CrX(CO)_5$ ($X = Cl^-$, Br^-) were used, no reaction occurred, and it was suggested that the steric crowding expected in a triple iodo bridged complex and the reluctance of a first row transition metal to be seven co-ordinate were the reasons for this lack of reaction.[81]

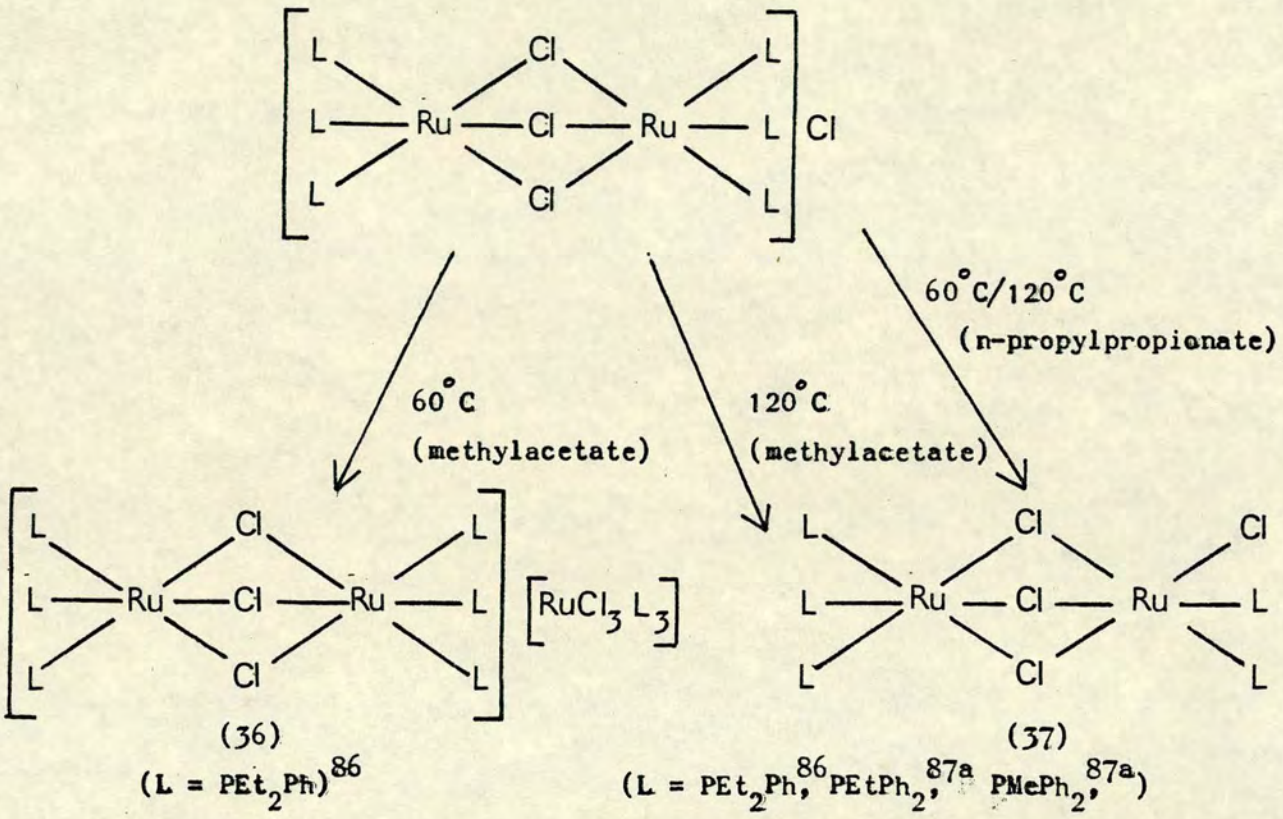
The complexes (35) reacted with pyridine[81] to give the compounds $MoY(\eta^3\text{-allyl})(CO)_2(py)_2$ analogous to the tungsten complex (33). Although metathetical reactions of the complex (35) ($Y = Cl^-$) with LiI to produce the triple iodide bridged compound were unsuccessful, reactions with $NaOH/ROH_{(aq)}$, $Na_2CO_3/ROH_{(anhy)}$ (R = Me, Et) and $Na_2CO_3/PhSH$ gave the complexes (35) ($Y = OMe^-$, OEt^- and SPh^-) respectively.[81] The compound (35) ($Y = OH^-$) was prepared by the reaction of (35) ($Y = Cl^-$) with $[Et_4N]OH$.[82]

1.7 Complexes containing Group 5B donor ligands:

The first report of triple bridged complexes containing group 5B donor ligands was in 1961 when Chatt and Hayter[83] synthesised the compounds $[M_2(\mu\text{-}Cl)_3L_6]Y$, (M = Ru or Os; L = PEt_2Ph, PMe_2Ph, $PMePh_2$, $PEtPh_2$; Y = Cl^-, ClO_4^-, SCN^-, BPh_4^-, picrate). These complexes were formed by the reaction of "$RuCl_3xH_2O$" or $Na_2[OsCl_6]$ respectively with the appropriate phosphine in either methanol or ethanol. They were initially isolated for $Y = Cl^-$ and the other derivatives were prepared by reaction of these with the appropriate anion. The analogous complexes $[Ru_2(\mu\text{-}X)_3L_6]Y$, ($X = Y = Cl^-$, $L = P^nPr_2Ph$, P^nBu_2Ph; $X = Cl^-$, $L = PEt_3$, $Y = BPh_4^-$; $X = Y = Br^-$, I^-, $L = PMe_2Ph$) have also been reported.[84] The formulation of the cation in these complexes was shown to be correct in 1969 when the X-ray analysis of the compound $[Ru_2(\mu\text{-}Cl)_3(PEt_2Ph)_6]$-$[RuCl_3(PEt_2Ph)_3]$ (36) was reported.[85] Complex (36) and the neutral compound $Ru_2(\mu\text{-}Cl)_3Cl(PEt_2Ph)_5$ (37) were prepared by the pyrolysis of $[Ru_2(\mu\text{-}Cl)_3(PEt_2Ph)_6]Cl$ in either methylacetate or n-propylpropionate[86] (see Fig. 1.10.).

Fig. 1.10.

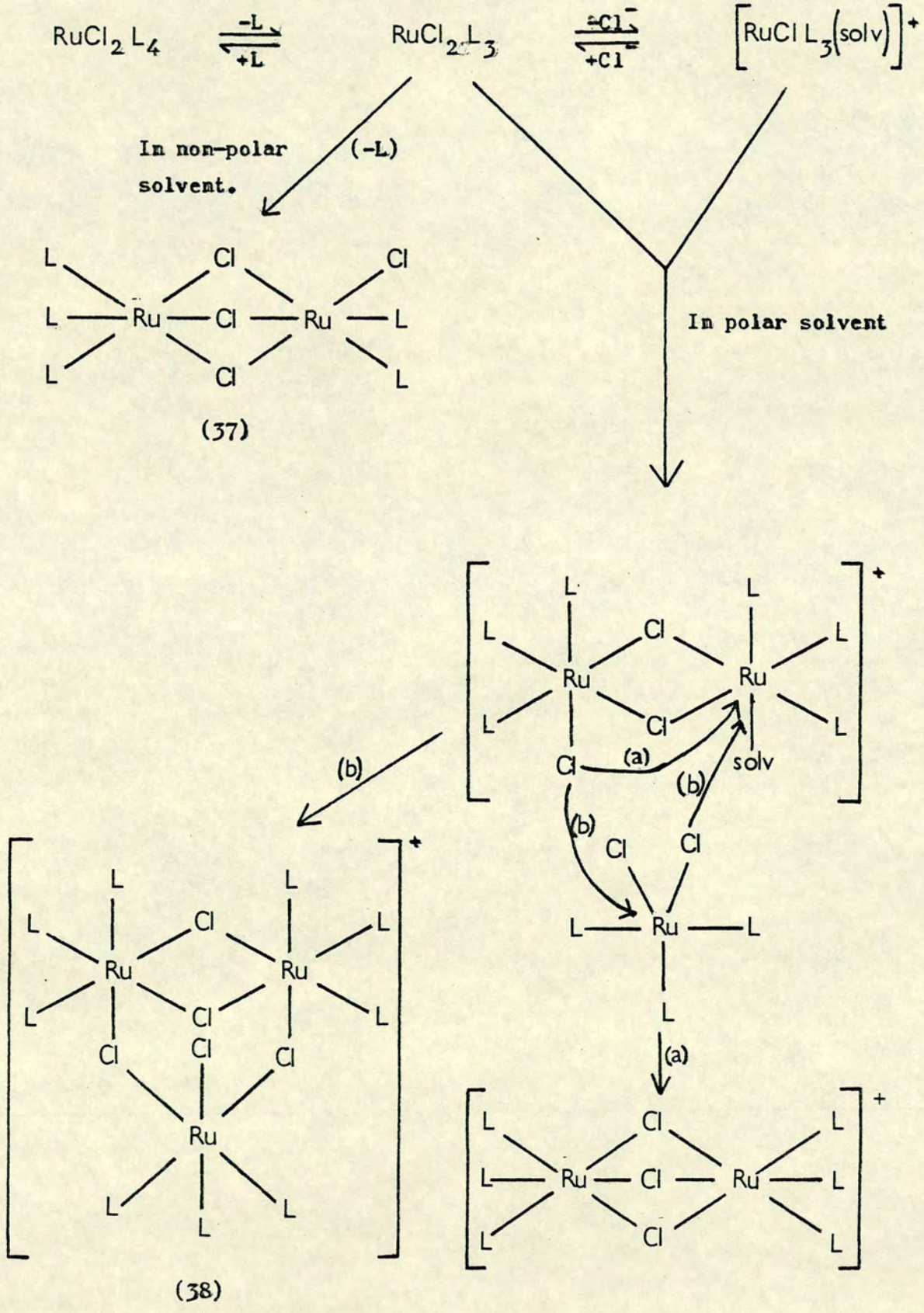
Pyrolysis of $[Ru_2(\mu\text{-}Cl)_3L_6]Cl$



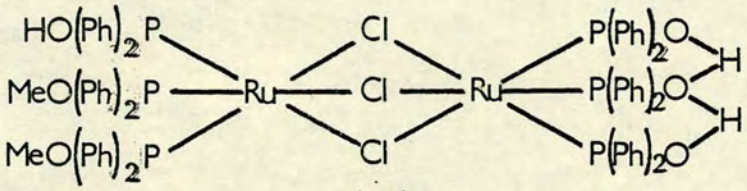
The complexes (37) (L = $PMePh_2$, $PEtPh_2$) were later prepared similarly,[87a] and these types of compound can also be synthesised starting from the monomers $RuCl_2L_3$ or 4.[87b,88,89a] Electrochemical studies on these neutral molecules are described in Chapter 4. The overall rearrangement process of these reactions is shown in Fig. 1.11. When L = tertiary phosphine, (except for PMe_2Ph), both $[Ru_2(\mu\text{-}Cl)_3L_6]Y$ and complex (37) can be isolated: however, when L = tertiary phosphonite, phosphinite, phosphite or PMe_2Ph, only the cationic complexes $[Ru_2(\mu\text{-}Cl)_3L_6]Y$ and, in one case, the trinuclear complex (38) (L = $P(OEt)Ph_2$) are formed.[88,90] Attempts to synthesise complexes of type

Fig. 1.11.

Rearrangement of the complexes $RuCl_2L_{3 \text{ or } 4}$ in polar and non-polar solvents.

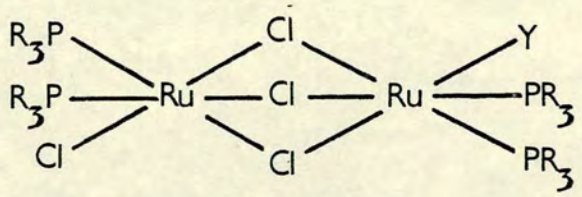


(37) for L = tertiary phosphonite, phosphinite, phosphite and PMe_2Ph by pyrolysis of the corresponding cationic complexes failed, and this was attributed to the greater strength of the Ru-P bonds in these complexes, compared to those containing tertiary phosphines. In support of this, pyrolysis of the complex $\left[Ru_2(\mu\text{-}Cl)_3(P(OMe)Ph_2)_6\right]Cl$ gave compound (39) in which all Ru-P bonds are retained, and preferential bond rupture of some O-R bonds has occurred.[91]



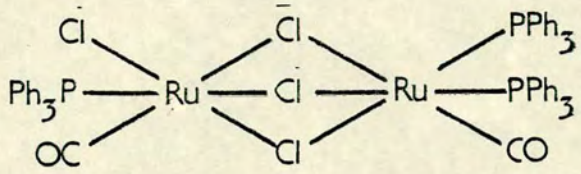
(39)

Recently the reactions of the complexes $RuCl_2(PR_3)_2Y(dmf)$ (R = Ph, p-tolyl, Y = CO, CS) with the corresponding compounds $RuCl_2(PR_3)_3$ have been investigated, and the binuclear complexes (40) isolated.[89a,b,91] The structure of compound (40) (R = Ph, Y = CS) was confirmed by X-ray crystallographic analysis.[93]

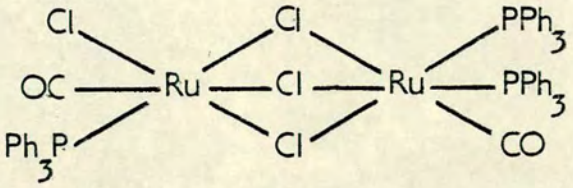


(40)

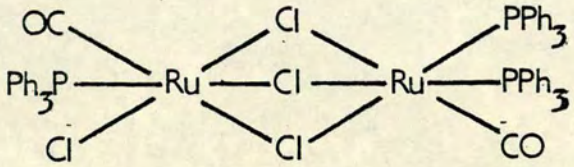
In addition, $RuCl_2(PPh_3)_2CO(MeOH)$ readily undergoes self dimerisation to give an isomeric mixture of complexes (41) (a), (b), and (c) as shown by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy.[89a]



(41a)

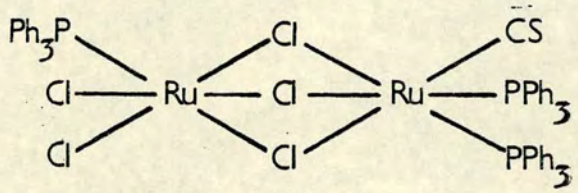


(41b)



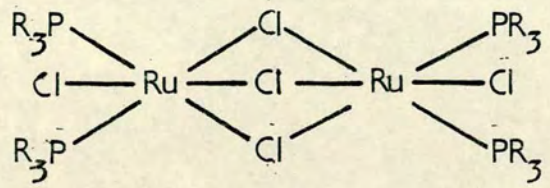
(41c)

The reaction of complex (40) (R = Ph, Y = CS) with conc. HCl in acetone gave the mixed valence compound (42).[92] This reaction presumably occurs via protonation of PPh_3 and subsequent loss of Ph_3PH^+ followed by addition of Cl^- (see Chapter 4 for further discussion).



(42)

There has been one other report of similar mixed valence compounds namely $Ru_2(\mu\text{-}Cl)_3Cl_2(PR_3)_4$ (R = ^{n}Bu, ^{n}Pent) which are formed in the reaction of "$RuCl_3.xH_2O$" with the appropriate phosphine.[94] An X-ray analysis[95] for (R = ^{n}Bu) confirmed the proposed configuration (43).

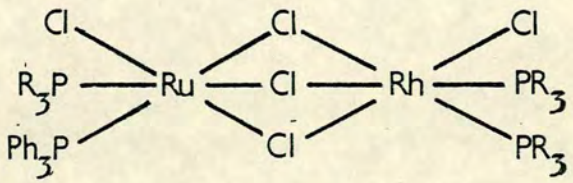


(43)

The reactions of $RuCl_2(PPh_3)_3$ with PF_3 and $P(NMe_2)F_2$ have recently been reported[96] and the compounds (44) (L = PF_3), (45a) and (45b) isolated. Surprisingly, the compound (45a) (L = PF_3) was also formed by the coupling reaction of $RuCl_2(PPh_3)_3$ and <u>cis</u>-$RuCl_2(PF_3)_2(PPh_3)_2$, showing that ligand transfer occurs. However, the reaction with <u>cis</u>-$RuCl_2(P(NMe_2)F_2)_2(PPh_3)_2$ gives the expected product (46) without ligand transfer (see Figs. 1.12 and 1.13). This is thought to reflect the ease of dissociation of PPh_3 from <u>cis</u>-$RuCl_2(P(NMe_2)F_2)_2(PPh_3)_2$ as opposed to that from <u>cis</u>-$RuCl_2(PF_3)_2(PPh_3)_2$.

The reaction of the compound $RuH_2CO(PPh_3)_3$ with HCl in benzene[96] gives an isomeric mixture of the previously reported[89a] complex $Ru_2(\mu\text{-}Cl)_3Cl(PPh_3)_3(CO)_2$ (41) and the reaction of the compound $Ru_2(\mu\text{-}Cl)_3Cl(PPh_3)_4CO$ (40) with PF_3 gives the complex $Ru_2(\mu\text{-}Cl)_3Cl(PPh_3)_3(CO)PF_3$ as a mixture of two of the three possible isomers.

The same group of workers also reported[97] the syntheses of the heteronuclear complexes (47), formed by the reaction of $RuCl_2(PPh_3)_3$ and <u>mer</u>-$RhCl_3(PR_3)_3$ (PR_3 = PMe_2Ph, PEt_2Ph, P^nBu_3, P^nBu_2Ph, PPh_3) (1:1 molar ratio) and again, ligand transfer has occurred.



(47)

Fig. 1.12.

Reactions of $RuCl_2(PPh_3)_3$ with PF_3 and $P(NMe_2)F_2$.

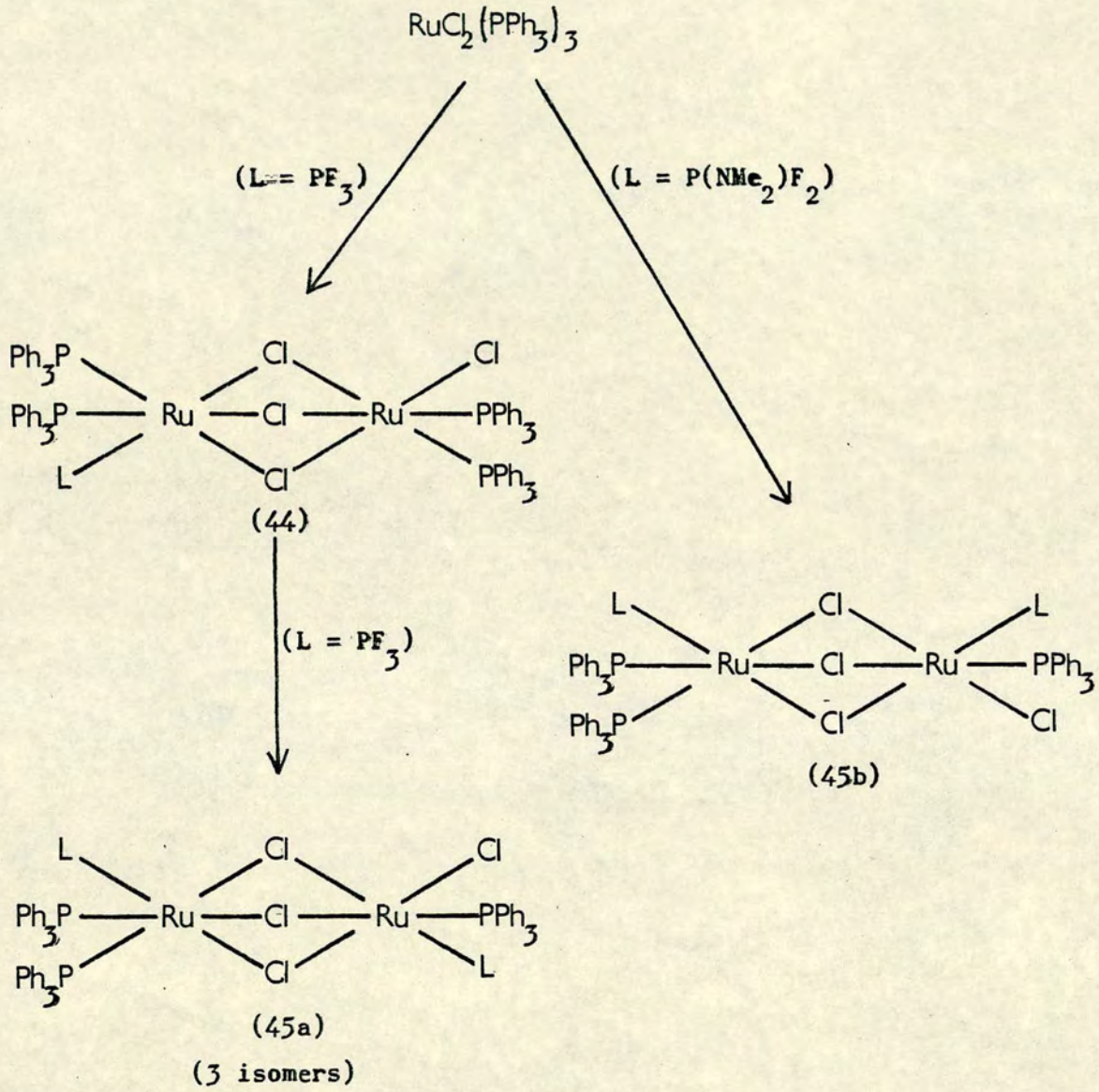
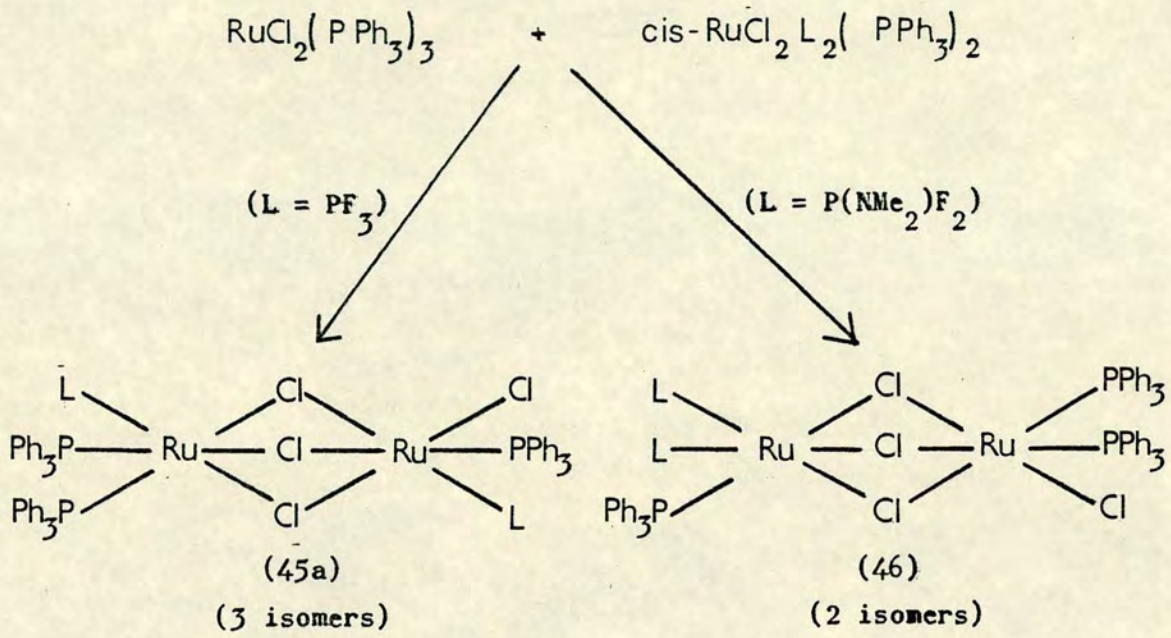


Fig. 1.13.

Coupling reactions of $RuCl_2(PPh_3)_3$ with cis-$RuCl_2L_2(PPh_3)_2$.



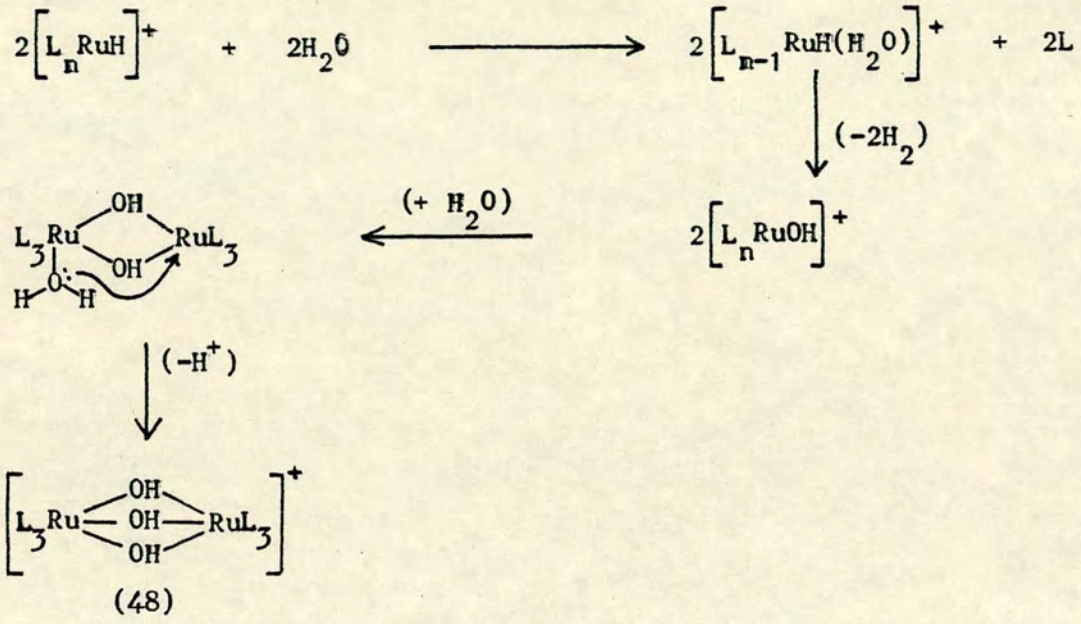
A brief communication[98] on the reactions of the compounds $[RuH(cod)L_3]PF_6$ (L = PMe_2Ph, $PMePh_2$, $P(OMe)Ph_2$) with the acids HX ($X = OH^-$, SH^-, SMe^-, Cl^-, Br^-, I^-, F^-) reports the formation of the complexes $[Ru_2(\mu\text{-}X)_3L_6]Y$, ($X = OH^-$, L = PMe_2Ph, $PMePh_2$, $P(OMe)Ph_2$; $X = F^-$, SH^-, SMe^-, L = PMe_2Ph; $X = Cl^-$, Br^-, L = PMe_2Ph, $PMePh_2$; $Y = PF_6^-$ or BPh_4^-). The compound ($X = H^-$) was also isolated from the reaction of $[Ru(O_2CH)(PMe_2Ph)_4][PF_6]_2$ with methanol. The formulation of these complexes as containing triple bridged binuclear cations was confirmed by the crystal structure determination[98] of (48) (L = PMe_2Ph, $Y = BPh_4^-$).

The proposed mechanism for the formation of the compound (48) ($X = OH^-$) is shown in Fig. 1.14. Thus, the interaction of a basic ruthenium hydrido species with a weak acid leads to loss of H_2 followed by deprotonation of, for example, a ruthenium aquo species,

to give the product (48).

Fig. 1.14.

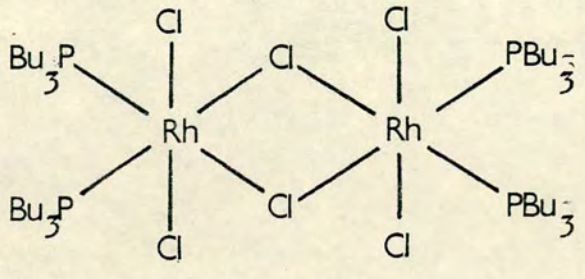
Proposed mechanism for the formation of $[Ru_2(\mu\text{-}OH)_3L_6]^+$



(48)

The triple bridged complex $Ru_2(\mu\text{-}X)_3X(NCR)(cod)_2$ was also isolated from the reaction of $RuX_2(cod)(NCR)_2$ ($X = Cl^-$, Br^-; R = Me, Et) with methanol.

Rhodium and Iridium Complexes: Chatt and co-workers[99] investigated the reactions of $RhCl_3.3H_2O$ with tertiary phosphines and arsines and reported the synthesis of two types of binuclear compound $Rh_2(\mu\text{-}Cl)_3Cl_3(ER_3)_3$ (E = P, As, R = Et) and $Rh_2(\mu\text{-}Cl)_2Cl_4(ER_3)_4$ (E = P, R = ^{n}Pr, ^{n}Bu, ^{n}Pent; E = As, R = Et). The double bridged compound (E = P, R = ^{n}Bu) was assigned the structure (49a) on the basis of $^{31}P\text{-}\{^1H\}$ n.m.r. data.[100]

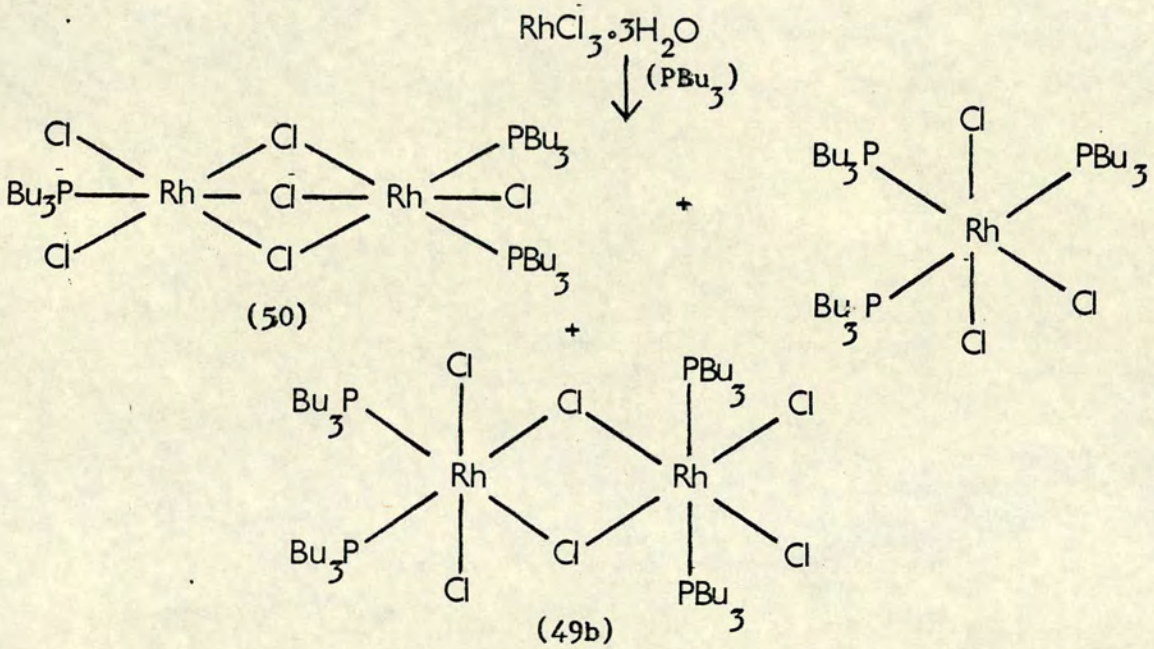


(49a)

However, this structure was inconsistent with the observed high dipole moment, and a reinvestigation[101] of the reaction showed that the product was actually a mixture of the three complexes (49b), (50) and mer-$RhCl_3(PBu_3)_3$ (see Fig. 1.15).

Fig. 1.15.

Reaction of $RhCl_3 \cdot 3H_2O$ with PBu_3.

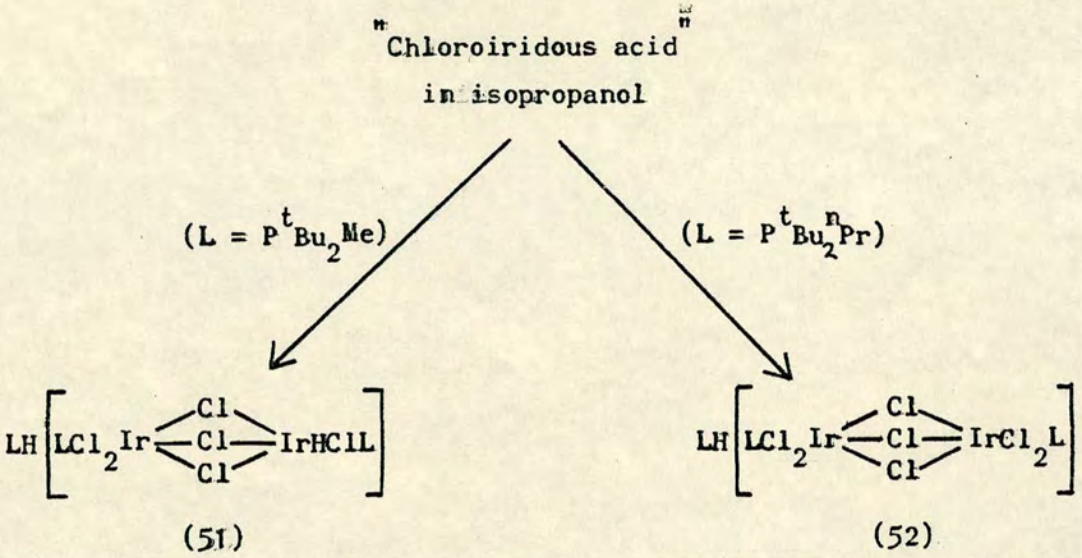


The structure of (49b) is now consistent with the high dipole moment observed and the configurations of (50)[102] and (49b)[103] were later confirmed by X-ray analysis. The rhodium (III) complexes of type (50) react with excess phosphine to give the double bridged compounds of type (49b).

The triple chloride bridged iridium (III) complexes (51) and (52) have been prepared[104] by the reaction of "chloro-iridous" acid with the appropriate phosphine in iso-propanol (see Fig. 1.16).

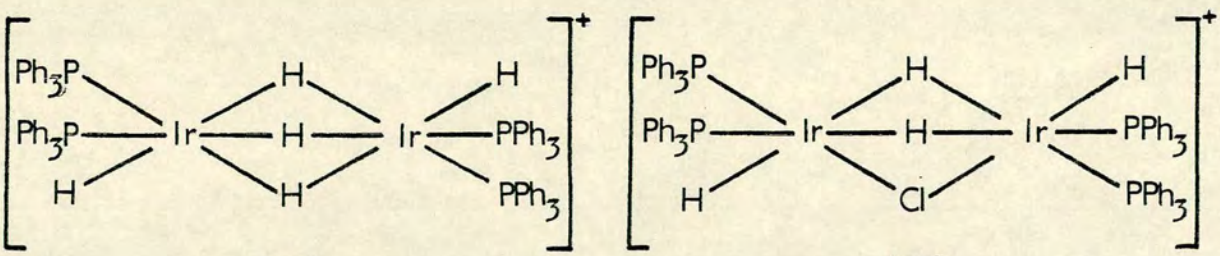
Fig. 1.16.

Synthesis of the complexes $LH[Ir_2(\mu\text{-}Cl)_3Cl_3HL_2]$ (51) and $LH[Ir_2(\mu\text{-}Cl)_3Cl_4L_2]$ (52).



(51) (52)

A triple hydrido bridged complex of iridium (III) has also been synthesised.[105,106] Thus, the reaction of $[Ir(cod)(PPh_3)_2]PF_6$ with H_2 in CH_2Cl_2/toluene at 0°C gave the cation (53) which, on reaction with conc. HCl gave $[Ir_2(\mu\text{-}H)_2(\mu\text{-}Cl)(H)_2(PPh_3)_4]^+$ (54). The structures of (53) and (54) were deduced from $^{31}P\text{-}\{^1H\}$ and ^1H n.m.r. studies, and an X-ray structure of (54) with PF_6^- as the counterion later confirmed this assignment.[106]

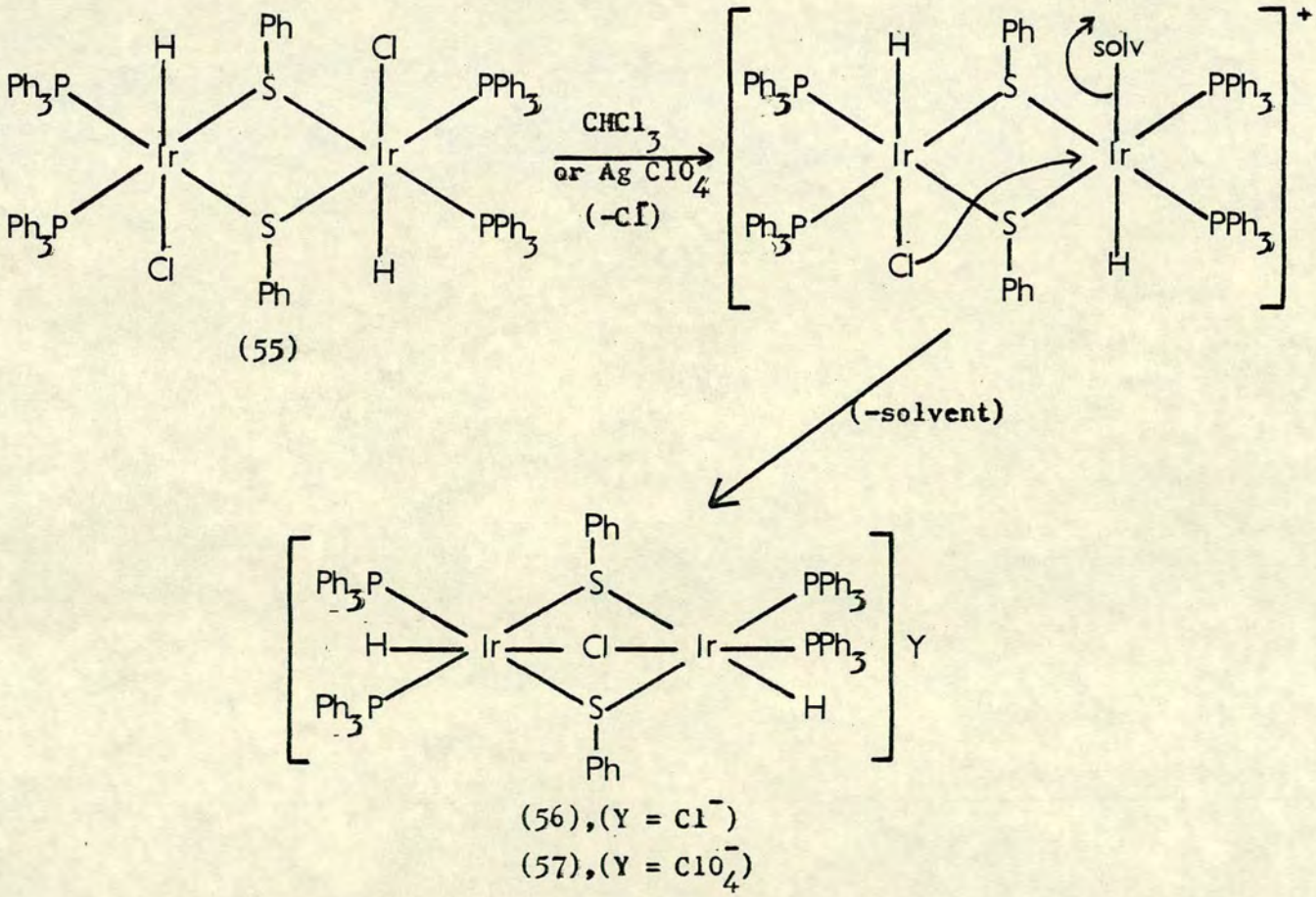


(53) (54)

One other triple bridged complex of iridium has been reported.[107] It was observed that the double bridged complex (55) slowly dissolved in halogenated hydrocarbons such as $CHCl_3$ or $C_2H_4Cl_2$ to give a yellow solution from which a white solid analysing for $Ir_2(SPh)_2Cl_2(H)_2(PPh_3)_4$ (56) could be isolated. The reaction of (55) with $Ag[ClO_4]$ also gave a white solid which was formulated as the chloro-thiophenol bridged complex (57). Thus, the reaction of compound (55) is thought to proceed by the pathway shown in Fig. 1.17, and the structure of complex (57) was confirmed by X-ray crystallography.[107]

Fig. 1.17.

Proposed mechanism for the reaction of $Ir_2(\mu\text{-}SPh)_2Cl_2H_2(PPh_3)_4$ (55) with halogenated hydrocarbons and $Ag[ClO_4]$.

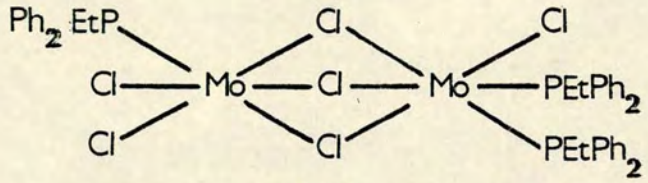


(55)

(56), (Y = Cl^-)

(57), (Y = ClO_4^-)

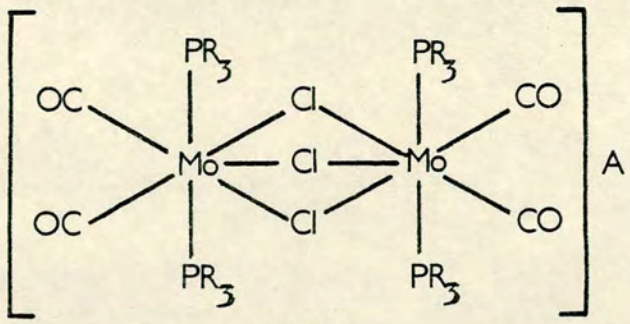
Molybdenum: The molybdenum (III) complexes $Mo_2(\mu\text{-}Cl)_3Cl_3L_3$ (L = $PEtPh_2$, PPh_3, C_5H_5N, P(cyclohexyl)$_3$) have been synthesised.[108,109] For example, the compound mer-$MoCl_3(thf)_3$ reacts with neat $PEtPh_2$ to give complex (58). However, reaction with other phosphines or pyridine gives the monomeric compounds $MoCl_3L_n(thf)_{3-n}$ (n = 3, L = PMe_2Ph, PEt_2Ph, P^nPr_2Ph, P^nBu_2Ph, $PMePh_2$, py); n = 2, L = $PMePh_2$, $PEtPh_2$; py; n = 1, L = PEt_2Ph, $PEtPh_2$ py).



(58)

The compound $MoCl_5$ reacts with MeCN to give the complex analogous to (58) with co-ordinated MeCN instead of phosphine, and this complex then reacts with PPh_3, P(cyclohexyl)$_3$ or pyridine to produce the corresponding tertiary phosphine and pyridine compounds.[109]

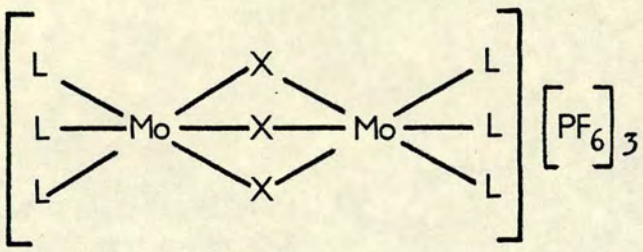
A recent report[110] on the reactions of cis-$Mo(CO)_3(PR_3)_3$ (R = OMe, ^nBu, Ph) with $SbCl_5$ or $FeCl_3$ has shown that the triple chloro bridged complexes (59) (A = $SbCl_6^-$, $FeCl_4^-$) were formed, which are examples of seven co-ordinate molybdenum (II).



(59)

Compound (59) (R = OMe) reacts with P^nBu_3 with cleavage of the bridges to give the compounds $MoCl_2(P^nBu_3)_n(P(OMe)_3)_{3-n}(CO)_2$ (n = 1-3) by stepwise displacement of $P(OMe)_3$.

Finally, the reaction of the cation $[(\eta^6\text{-}C_6H_5R)Mo(py)_3]^+$ (R = Me) with MeSH in aqueous methanol followed by extraction of the residue with acetone/HPF_6 gives a novel quadruply bridged complex $[Mo_2(\mu\text{-}SMe)_4(\eta^6\text{-}C_6H_5R)_2][PF_6]_2$, which when reduced with zinc amalgam in 1-methylimidazole/acetonitrile solution gave the triple bridged compound (60). (X = SMe^-, L = ). [111]



(60)

<u>Iron and Cobalt:</u> The complexes $[M_2(\mu\text{-}H)_3(E_3)_2]X$, (M = Fe, E_3 = $CH(CH_2\text{-}PPh_2)_3$; M = Co, E_3 = $CH(CH_2\text{-}PPh_2)_3$ or $CH(CH_2AsPh_2)_3$; X = PF_6^- or BPh_4^-) have been synthesised by the reaction of Fe(II) or Co(II) salts with $NaBH_4$ in the presence of E_3 and bulky anions PF_6^- or BPh_4^-. The formulation as triple hydrido bridged cations was confirmed by X-ray analysis of the compound (M = Fe, X = BPh_4^-). [112]

Chapter 2

The Syntheses of Some New Triple Halo-Bridged Arene Complexes of Ruthenium(II) and Osmium(II)

2.1 Introduction

As described earlier (section 1.4), Bennett and Smith reported the synthesis of the compounds $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-arene})_2\right]PF_6$ (9a) (arene = C_6H_6) and (9b) (arene = p-Me-$C_6H_4CH(Me)_2$) in 41% and 68% yield respectively. However, repetition of this reaction (for arene = C_6H_6) in our laboratories gave consistently lower yields (10-20% of complex (9a) and in one case an amine-containing compound which was shown by X-ray analysis to be $\left[RuCl(NH_3)_2(\eta^6\text{-}C_6H_6)\right]_3(PF_6)_3 \cdot NH_4PF_6$. By analogy with the work of Maitlis who isolated the isoelectronic compound $\left[Rh_2(\mu\text{-}Cl)_3(\eta^5\text{-}C_5Me_5)_2\right]BPh_4$ (8a), it was found that shaking the complex $\left[RuCl_2(\eta^6\text{-}C_6H_6)\right]_2$ in methanol with a slight excess of NH_4PF_6 gave the complex (9a) in high yield (ca 90%). Unfortunately this route was found not to be a general one, since the reaction of NH_4PF_6 with other complexes $\left[RuX_2(\eta^6\text{-arene})\right]_2$ ($X = Br^-$, I^-, arene = C_6H_6; $X = Cl^-$, arene = 1,3,5-$C_6H_3Me_3$) produced only the unreacted starting materials.

This chapter describes and discusses new synthetic routes to triple halo bridged complexes analogous to (9a), via the protonation of equimolar concentrations of the monomeric compounds $MX_2(\eta^6\text{-arene})py$ ($M = Ru$, $X = Cl^-$, Br^-, arene = C_6H_6; $M = Ru$, $X = Cl^-$, I^-, arene = 1,3,5-$C_6H_3Me_3$) and $\left[MX(\eta^6\text{-arene})(py)_2\right]PF_6$ ($M = Ru$, $X = Cl^-$, Br^-, arene = C_6H_6; $M = Ru$, $X = Cl^-$, Br^-, I^-, arene = 1,3,5-$C_6H_3Me_3$; $M = Os$, $X = Cl^-$, arene = C_6H_6).

2.2 A brief history of the synthesis and reactions of the compound $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2\right]PF_6$ (9a).

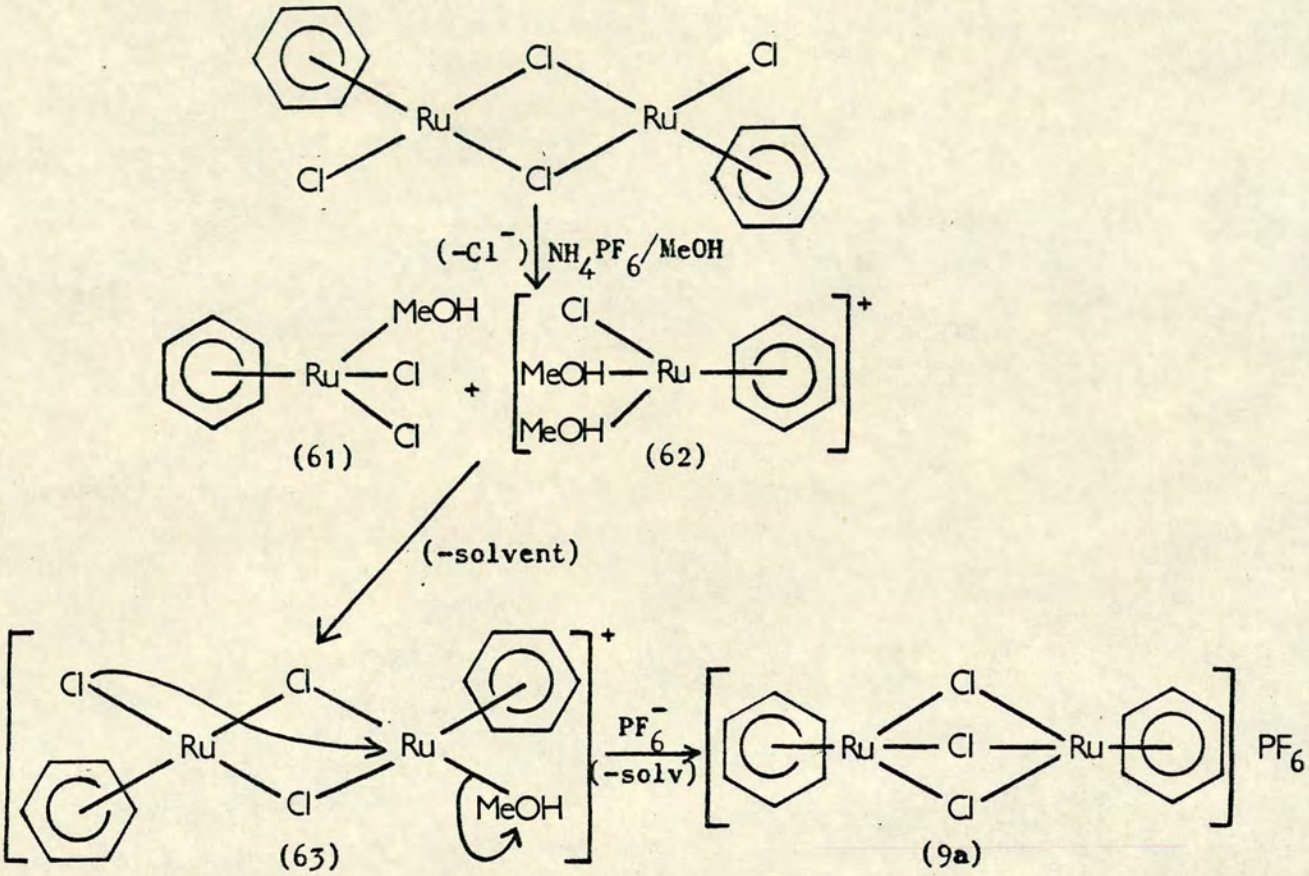
The reaction of the compound $\left[RuCl_2(\eta^6\text{-}C_6H_6)\right]_2$ with NH_4PF_6 in methanol has been postulated to proceed via the initial formation of the solvated monomers (61) and (62) which then couple together to

form the triple bridged complex (9a) either directly or via a double bridged intermediate (63) (see Fig. 2.1). A similar mechanism has been postulated for the formation of the complexes $[Ru_2(\mu\text{-}Cl)_3L_6]Cl$ ($L = PR_3$, $P(OR)R_2$, $P(OR)_2R$, $P(OR)_3$) (see Fig. 1.11 p.30). Although no evidence for the solvated monomers (61) and (62) has been observed in methanol probably because of the low solubility of $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ in this medium, similar species have been shown to be present in other solvents such as D_2O and d^6-dmso by ^1H n.m.r. spectroscopic studies.[113] It is thought that the even greater insolubility of the complexes, $[RuX_2(\eta^6\text{-arene})]_2$ ($X = Br^-$, I^-, arene = C_6H_6; $X = Cl^-$, arene = 1,3,5-$C_6H_3Me_3$) in methanol and hence the failure to generate sufficient concentrations of monomers analogous to (61) and (62) is the reason why these compounds do not form the corresponding triple bridged cations on reaction with NH_4PF_6 in methanol.

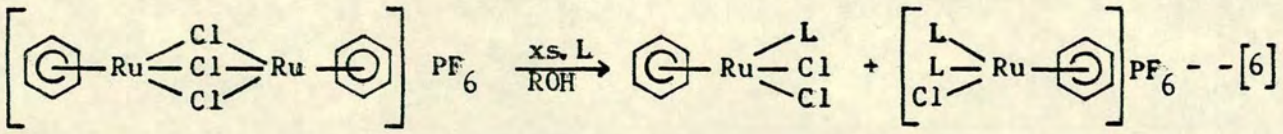
Complex (9a) was found to undergo facile bridge cleavage reactions in solution with the production of various monomeric species. Thus, in D_2O, the ^1H n.m.r. spectrum shows two resonances due to co-ordinated benzene at δ = 6.39 ppm. and 6.50 ppm. which were assigned to the species $RuCl_2(\eta^6\text{-}C_6H_6)D_2O$ and $[RuCl(\eta^6\text{-}C_6H_6)(D_2O)_2]^+$ respectively, whereas in d^6-Me_2SO, a stronger co-ordinating solvent, three resonances were observed at δ = 5.95 ppm., 6.15 ppm. and 6.50 ppm. which were assigned to $RuCl_2(\eta^6\text{-}C_6H_6)(d^6\text{-}Me_2SO)$, $[RuCl(\eta^6\text{-}C_6H_6)(d^6\text{-}MeSO)_2]^+$ and $[Ru(\eta^6\text{-}C_6H_6)(d^6\text{-}Me_2SO)_3]^{2+}$ respectively.[113] Complex (9a) was also soluble in $MeNO_2$ and since it behaved as a 1:1 electrolyte in this medium this suggested that it remains intact in this solvent. A later investigation (this work) of both the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra in d^3-$MeNO_2$ which showed only one resonance at δ = 5.93 ppm. and 82.0 ppm. respectively, attributable to the magnetically equivalent $\eta^6\text{-}C_6H_6$ rings in (9a), supports this conclusion.

Fig. 2.1.

Proposed mechanism for the formation of $[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2]PF_6$



Compound (9a) was found to react in ROH (R = Me, Et) with various Lewis bases (L) to give the cationic complexes $[RuCl(\eta^6\text{-}C_6H_6)L_2]PF_6$ (L = PPh_3, $AsPh_3$, PMe_2Ph, Et_2S, C_5H_5N etc,) and the neutral compounds $RuCl_2(\eta^6\text{-}C_6H_6)L$[113]. Hence, asymmetric cleavage of (9a) has occurred as shown in eqn. [6].



2.3 Syntheses and characterisation of the monomeric compounds $MX_2(\eta^6\text{-arene})py$ and $[MX(\eta^6\text{-arene})(py)_2]PF_6$.

The proposed reaction scheme shown in Figure 2.1 for the formation of compound (9a) involves the production of the solvated monomers (61) and (62) and it was therefore considered that a good way of synthesising other complexes analogous to (9a), namely, $[Ru_2(\mu\text{-}X)_3(\eta^6\text{-arene})_2]Y$ ($X = Cl^-$, Br^-, I^- etc; arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, etc.; $Y = BF_4^-$ or PF_6^-), would be by in situ generation of complexes analogous to (61) and (62). It was thought that this might be accomplished by reaction of an equimolar mixture of $RuX_2(\eta^6\text{-arene})L$ and $[RuX(\eta^6\text{-arene})L_2]PF_6$ (where L is a ligand which can readily be protonated to give a good leaving group LH^+) with acids such as HBF_4 or HPF_6 which contain large, non-co-ordinating anions. Suitable complexes $RuCl_2(\eta^6\text{-}C_6H_6)py$[115] and $[RuCl(\eta^6\text{-}C_6H_6)(N\text{-}N)]PF_6$[116] (N-N = 2,2′ - bipyridyl or 1,10 - phenanthroline) had already been synthesised but the bidentate ligands (N-N) proved very difficult to protonate completely (see section 2.4), and hence these could not be used successfully.

The complex $[RuCl(\eta^6\text{-}C_6H_6)(py)_2]PF_6$ was known,[113] but since it had been synthesised from the triple bridged complex (9a), this route could not be used to generate the analogous compounds $[RuX(\eta^6\text{-arene})(py)_2]PF_6$ ($X = Br^-$, I^-, etc.) since the compounds $[Ru_2(\mu\text{-}X)_3(\eta^6\text{-arene})_2]PF_6$ were as yet unknown. However, it had been reported that the complex $[RuCl(\eta^6\text{-}C_6H_6)(en)]BPh_4$ (en = ethylenediamine) could be synthesised from the dimer $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ by reaction with a slight excess of ethylenediamine in methanol, followed by addition of excess $NaBPh_4$.[117] A similar reaction with pyridine followed by addition of NH_4PF_6 then gave the complex $[RuCl(\eta^6\text{-}C_6H_6)(py)_2]PF_6$ in high yield. This reaction was found to be quite general and the compounds $[MX(\eta^6\text{-arene})(py)_2]PF_6$ ($M = Ru$, $X = Br^-$, arene = C_6H_6; $M = Ru$, $X = Cl^-$, Br^-, I^-, arene =

1,3,5-$C_6H_3Me_3$ and M = Os, X = Cl, arene = C_6H_6, p-$MeC_6H_4CH(Me)_2$) were prepared similarly. However, more forcing reaction conditions were required when M = Ru, X = Br^-, arene = C_6H_6 or when M = Os, X = Cl^-, arene = C_6H_6, and this is probably mainly due to the increased stability of the corresponding compounds $\left[MX_2(\eta^6\text{-arene})\right]_2$ towards bridge cleavage. This is further emphasised by the failure to generate the compounds $\left[RuX(\eta^6\text{-}C_6H_6)(py)_2\right]PF_6$ (X = I^-, SCN^-) from the very insoluble complexes $\left[RuX_2(\eta^6\text{-}C_6H_6)\right]_2$, even under very vigorous conditions; eg. refluxing in ethanol with a very high concentration of pyridine present. Another reaction designed to synthesise these complexes, namely treatment of $\left[RuCl(\eta^6\text{-}C_6H_6)(py)_2\right]PF_6$ with a 1:1 molar ratio of $AgPF_6$ in MeOH to generate <u>in situ</u> the dication $\left[Ru(\eta^6\text{-}C_6H_6)(py)_2(sol)\right]^{2+}$, followed by addition of LiX (X = I^-, or SCN^-), also failed, since the products were identified as the dimeric complexes $\left[RuX_2(\eta^6\text{-}C_6H_6)\right]_2$. Presumably, the driving force for the formation of these dimers is their extreme insolubility.

The complexes $\left[RuX(\eta^6\text{-arene})(py)_2\right]PF_6$ were characterised by elemental analysis (C,H and N), (see Table 2.1), ir. spectra which showed the presence of pyridine and PF_6^- vibrations and ^1H n.m.r. spectroscopy in d^6-Me_2CO, the integration showing two co-ordinated pyridine ligands for each η^6-arene ring.

As shown in section 2.7, Table 2.2, there is an increase in chemical shift of the aromatic protons of the η^6-arene rings in the complexes $\left[RuX(\eta^6\text{-arene})(py)_2\right]PF_6$ as the halide changes from Cl^- to Br^- to I^-. A similar deshielding trend has been observed for the complexes $TiX_2(\eta^5\text{-}C_5H_5)_2$ (X = Cl^-, Br^-, I^-)[118] and this was attributed to the increase in double bond character of the M-X bond (the resonance effect). This suggests that the apparent electron-withdrawing power of the halides is in the order $I^- > Br^- > Cl^-$ which is the opposite of

that expected on a purely inductive effect, based on the electronegativity of the halide.

The compound $RuCl_2(\eta^6\text{-}C_6H_6)py$ was first synthesised by direct reaction of $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ with pyridine in a non-polar medium.[115] It is also formed as a very insoluble orange solid by reaction of $Cs[RuCl_3(\eta^6\text{-}C_6H_6)]$ with pyridine.[113] This first type of reaction has now been used successfully to produce the analogous complexes $RuX_2(\eta^6\text{-arene})py$ ($X = Br^-$, arene = C_6H_6; $X = Cl^-$, I^-, arene = 1,3,5-$C_6H_3Me_3$). However, although the reaction of $[OsCl_2(\eta^6\text{-}C_6H_6)]_2$ or $[RuX_2(\eta^6\text{-}C_6H_6)]_2$ ($X = I^-$, SCN^-) with pyridine gave complexes which were shown to contain nitrogen and their ir. spectra indicated the presence of co-ordinated pyridine (ν(C = N) <u>ca.</u> 1600 cm^{-1}), elemental analyses (C,H and N) did not fit for the complexes $MX_2(\eta^6\text{-}C_6H_6)py$. Further studies indicate that the products are inseparable mixtures of the starting materials and the desired mono-pyridine complexes.

The complexes $RuX_2(\eta^6\text{-arene})py$ were characterised by analyses (C,H and N) (see section 2.7, Table 2:1), ir. spectra, which showed the presence of co-ordinated pyridine (see experimental section 2.7) and for arene = 1,3,5-$C_6H_3Me_3$, the compounds were sufficiently soluble in $CHCl_3$ to allow their ^1H n.m.r. spectra to be recorded. Integration of the ^1H n.m.r. resonances confirmed the presence of one co-ordinated pyridine ligand for each $\eta^6\text{-}C_6H_3Me_3$ ring. As was observed for the corresponding bis-pyridine complexes, there is an increase in chemical shift of the aromatic protons in the order $I^- > Br^- > Cl^-$ and a similar explanation can be invoked.

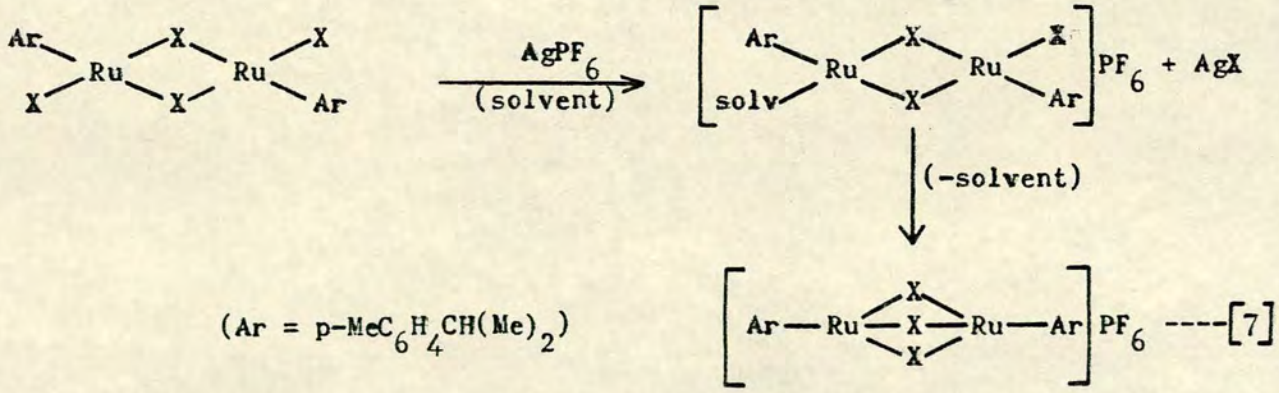
2.4 Syntheses and characterisation of the symmetric triple bridged complexes $[M_2(\mu\text{-}X)_3(\eta^6\text{-arene})_2]Y$, (M = Ru; X = Cl^-, Br^-, Y = BF_4^-, arene = C_6H_6; X = Cl^-, Br^-, I^-, arene = C_6H_6, p-Me-$C_6H_4CH(Me)_2$, Y = PF_6^-; X = Cl^-, Br^-, I^-, arene = 1,3,5-$C_6H_3Me_3$, Y = BF_4^-; M = Os, X = Cl^-, arene = C_6H_6, Y = BF_4^-).

The reaction of $RuCl_2(\eta^6\text{-}C_6H_6)py$ and $[RuCl(\eta^6\text{-}C_6H_6)(bipy)]PF_6$ (1:1 molar ratios) with HBF_4 in methanol gave, after removal of the solvent, an orange solid, shown by elemental analysis to contain small amounts of nitrogen. The ^1H n.m.r. spectrum in d^3-$MeNO_2$ contained a strong signal at δ = 5.93 ppm. and a much smaller one at 6.30 ppm. which were assigned to the triple bridged cation $[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2]^+$ and some unreacted $[RuCl(\eta^6\text{-}C_6H_6)(bipy)]^+$ cation respectively. Furthermore, the yield of the product mixture was quite low and attempts to obtain the triple bridged complex in a pure state were unsuccessful. However, when $[RuCl(\eta^6\text{-}C_6H_6)(py)_2]PF_6$ was used in place of $[RuCl(\eta^6\text{-}C_6H_6)(bipy)]PF_6$, the reaction gave the triple bridged complex $[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2]BF_4$ in almost quantitative yield and in an analytically pure state. The mull ir. spectrum of this complex was similar to that previously obtained for the compound (9a)[113] except for the bands attributable to BF_4^- as opposed to PF_6^-. The ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra in d^3-$MeNO_2$ at ambient temperature showed single resonances at δ = 5.93 ppm. and 82.0 ppm. respectively attributable to the $\eta^6\text{-}C_6H_6$ groups (cf. the PF_6^- complex which showed ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. signals at δ = 5.93 ppm. and 82.0 ppm. respectively). The analogous complexes $[Ru_2(\mu\text{-}X)_3(\eta^6\text{-arene})_2]BF_4$ (X = Br^-, arene = C_6H_6; X = Cl^-, I^-, arene = 1,3,5-$C_6H_3Me_3$) were prepared and characterised similarly (see experimental section 2.7 and Tables 2.3 and 2.4).

The complex $[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_3Me_3)_2]BF_4$ was also characterised

by detailed conductivity measurements which showed that the molar conductance (Λ_m) in $MeNO_2$ was 90.5 $ohm^{-1}cm^2mol^{-1}$, which lies within the range 75-95 $ohm^{-1}cm^2mol^{-1}$ expected for 1:1 electrolytes in this solvent.[119] Furthermore, a plot of $\Lambda_o - \Lambda_e$ vs. $C_e^{\frac{1}{2}}$ gave a straight line of slope 144 which is comparable to that obtained for other 1:1 electrolytes in $MeNO_2$ eg. $[Ru_2(\mu\text{-}Cl)_3(PEt_2Ph)_6]Cl$,[120] Λ_m = 85.5 $ohm^{-1}cm^2mol^{-1}$ slope, 151; $[Ru_2(\mu\text{-}Cl_3)(\eta^6\text{-}C_6H_6)_2]PF_6$,[113] Λ_m = 82 $ohm^{-1}cm^2mol^{-1}$; slope 207.

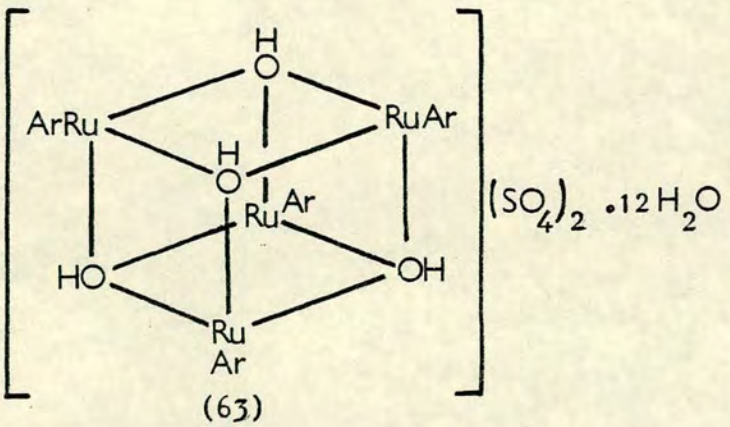
The observation that protonation of these monomers produces high yields of triple halide bridged arene cations provides direct evidence for the postulated mechanism shown in Fig. 2.1. It is not possible from these studies however, to determine unequivocally whether the triple halide bridged cation is formed by direct coupling of the solvated monomers or if a solvated, double halide bridged cation of type (63) is involved as a reaction intermediate. Good evidence that the latter is involved is provided by the observation that reaction of $[RuX_2(\eta^6\text{-p-cymene})]_2$ (X = Cl^-, Br^-, I^-) with $AgPF_6$ (1:1 molar ratio) in acetone gives $[Ru_2(\mu\text{-}X_3)(\eta^6\text{-p-cymene})_2]PF_6$ in reasonable yield (eqn. [7]).*



* Interestingly, attempts to synthesise these particular compounds starting from $RuX_2(\eta^6\text{-arene})py$, $[RuX(\eta^6\text{-arene})py_2]PF_6$ and HBF_4 were unsuccessful.

Similarly, $[Ru_2(\mu\text{-}I)_3(\eta^6\text{-}C_6H_6)_2]PF_6$ and $[Ru_2(\mu\text{-}Br)_3(\eta^6\text{-}C_6H_6)_2]PF_6$ were prepared by this route from $[RuX_2(\eta^6\text{-}C_6H_6)]_2$ and $AgPF_6$ in $MeNO_2$. The complex $[Ir_2(\mu\text{-}SPh)_2(\mu\text{-}Cl)(H)_2(PPh_3)_4]ClO_4$ (57) was synthesised in analogous fashion starting from $[IrHCl(\mu\text{-}SPh)(PPh_3)_2]_2$ and $AgClO_4$ (see Fig. 1.17, Chapter 1).[107]

Furthermore, since protonation of the compounds $[RuX(\eta^6\text{-arene})(py)_2]PF_6$ appears to generate the cations $[RuX(\eta^6\text{-arene})(solv)_2]^+$ *in situ*, it was hoped that in the absence of any $RuX_2(\eta^6\text{-arene})$-solv, intermediate,,these monomeric, solvated cationic intermediates would tetramerise with loss of co-ordinated solvent to give the novel cations $[RuCl(\eta^6\text{-arene})]_4^{4+}$. The expected driving force for these reactions would be the formation of six strong ruthenium ligand linkages since six co-ordinate Ru(II) is a highly favoured stereochemistry.[89a] A closely related complex $[Ru(OH)(\eta^6\text{-}C_6H_6)]_4(SO_4)_2.12H_2O$ with a cubane-like structure (63) has in fact been recently synthesised and one proposed mechanism of formation was by facile tetramerisation of a $[Ru(OH)(\eta^6\text{-}C_6H_6)(H_2O)_2]^+$ cation.[113,121] (see Chapter 3).



(63)

$(Ar = C_6H_6)$

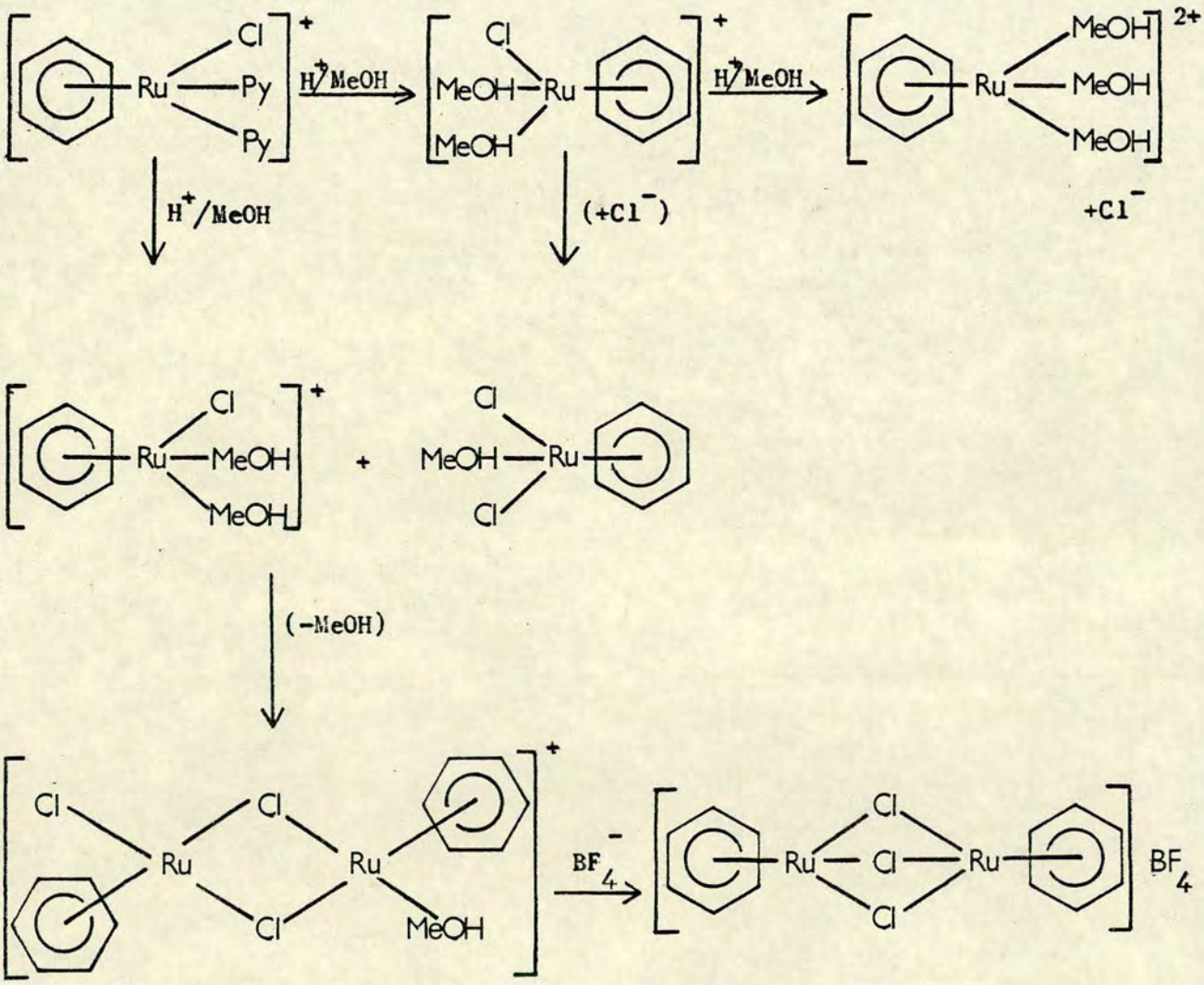
However, on reaction of $[RuCl(\eta^6\text{-}C_6H_6)py_2]PF_6$ with HBF_4 in methanol, the only product isolated was the triple bridged complex

$[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2]BF_4$. The failure of the cations $[RuCl(\eta^6\text{-}C_6H_6)(solv)_2]^+$ to tetramerise is perhaps not surprising since on simple coulombic ideas one would not expect four like charges to readily come together and form a complex of high overall charge.

However, the only way to rationlise the formation of this triply bridged cation is by the occurrence of facile chloride exchange, enhanced by the addition of acid. This will generate some of the neutral species $RuCl_2(\eta^6\text{-}C_6H_6)MeOH$ (61), which can then couple with the cation to give the triple bridged product (see Fig. 2.2). A "chloride deficient" product must also be formed but attempts to isolate this from solution were unsuccessful.

Fig. 2.2.

Postulated mechanism for the formation of $[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2]BF_4$ by protonation of $[RuCl(\eta^6\text{-}C_6H_6)(py)_2]PF_6$.



Although this facile chloride exchange probably prevents formation of any tetrameric cations, the reactions of the compounds $\left[MX(\eta^6\text{-arene})(py)_2\right]PF_6$ (M = Ru, X = Br^-, arene = 1,3,5-$C_6H_3Me_3$; M = Os, X = Cl^-, arene = C_6H_6) with HBF_4 can be used to synthesise low yields of the corresponding triple bridged complexes $\left[M_2(\mu\text{-}X)_3(\eta^6\text{-arene})_2\right]BF_4$. This is fortunate since the monopyridine compounds $MX_2(\eta^6\text{-arene})py$ (M = Ru, X = Br^-, arene = 1,3,5-$C_6H_3Me_3$; M = Os, X = Cl^-, arene = C_6H_6) could not be obtained in a pure state.(see section 2.3).

The reaction of the compound $\left[RuCl(\eta^6\text{-p-cymene})(py)_2\right]PF_6$ with HBF_4 in methanol, however, does not give the corresponding triple bridged complex. No products could in fact be isolated from the reaction mixture and this is probably due to the high solubility of all the Ru-(η^6-p-cymene) species.* A similar explanation can be proposed to explain why no products could be isolated from the reaction of the isoelectronic rhodium and iridium compounds $MX_2(\eta^5\text{-}C_5Me_5)py$ and $\left[MX(\eta^5\text{-}C_5Me_5)(py)_2\right]PF_6$ (M = Rh, Ir, X = Cl^-, I^-) with methanolic solutions of HBF_4.

2.5 Syntheses and characterisation of the mixed complexes, $\left[MM'(\mu\text{-}X)_2(\mu\text{-}X')(\eta^6\text{-arene})(\eta^6\text{-arene}')\right]BF_4$, M = M' = Ru, X = Cl^-, Br^-, X' = Br^-, Cl^-, arene = arene' = C_6H_6; M = M' = Ru, X = X' = Cl^-, arene = C_6H_6, arene' = 1,3,5-$C_6H_3Me_3$; M = Ru, M' = Os, X = X' = Cl^-, arene = arene' = C_6H_6).

Since the coupling reaction of $MX_2(\eta^6\text{-arene})py$ with $\left[MX(\eta^6\text{-arene})(py)_2\right]PF_6$ in HBF_4/MeOH was quite general and was limited only by the

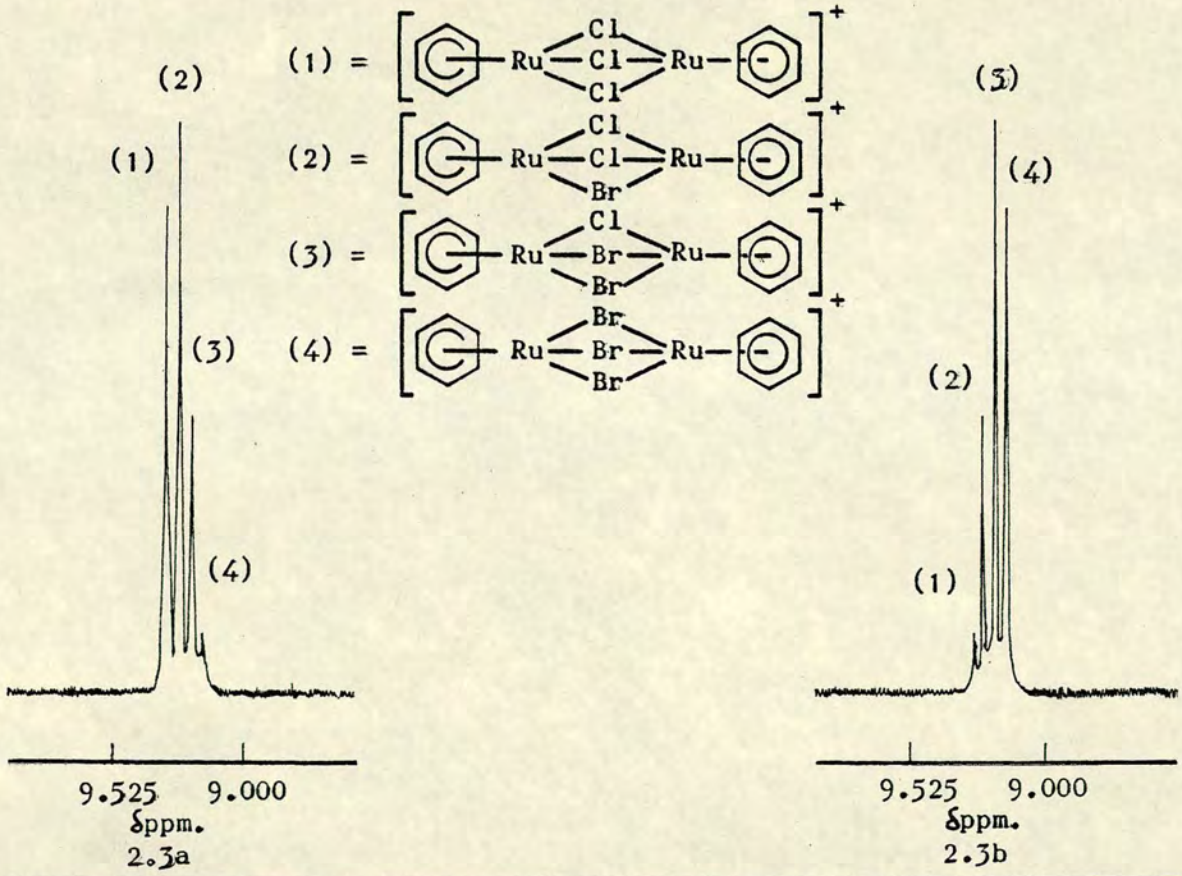
* As discussed earlier however, triple halide bridged cations containing this arene were isolated by treatment of $\left[RuX_2(\eta^6\text{-p-cymene})\right]_2$ with $AgPF_6$ in acetone.

availability of the two monomers, (or strictly speaking of only the cation), the possibility of using this route to synthesise hetero-bridged, hetero-arene and hetero-nuclear complexes was an obvious next step. Apart from some very recent examples of mixed triple halide bridged molybdenum complexes eg. $Mo_2(\mu\text{-}Cl)(\mu\text{-}Br)_2(\eta^7\text{-}C_7H_7)_2$[49,51] and the unsymmetric complexes $\eta^7\text{-}C_7H_7Mo(\mu\text{-}OR)_3Mo(\eta^3\text{-}C_7H_7)(CO)_2$[56] and $\eta^7\text{-}C_7H_7Mo(\mu\text{-}ER)_3Mo(CO)_3$ (E = S,Se)[57] (see Chapter 1, section 1.4), no successful general syntheses of such compounds have been previously reported. Therefore, a number of reactions were carried out to try and remedy this deficiency. Hence, the compounds $RuCl_2(\eta^6\text{-}C_6H_6)py$ and $\left[RuBr(\eta^6\text{-}C_6H_6)(py)_2\right]PF_6$ (1:1 molar ratio) were reacted together with HBF_4 in methanol and the product which was isolated in high yield analysed very closely (C,H,Cl,Br) for the mixed bridged complex $\left[Ru_2(\mu\text{-}Cl)_2(\mu\text{-}Br)(\eta^6\text{-}C_6H_6)_2\right]BF_4$. The ^1H n.m.r. spectrum in $d^3\text{-}MeNO_2$ on a wide spectral width (1000 Hz) showed a broadened resonance at δ = 5.93 ppm.. However, on narrower spectral widths (250 and 100 Hz) the resonance was seen to consist of several very closely separated peaks. A high resolution Fourier Transform ^1H n.m.r. spectrum at 298K showed four resonances at δ = 5.944 ppm., 5.937 ppm., 5.929 ppm., and 5.922 ppm., of relative intensity 8:12:6:1 (Fig. 2.3a). These were assigned to the $-(\mu\text{-}Cl)_3-$, $-(\mu\text{-}Cl)_2(\mu\text{-}Br)-$, $-(\mu\text{-}Cl)(\mu\text{-}Br_2-$ and $-(\mu\text{-}Br)_3-$ cations respectively, since the triple chloro and the triple bromo bridged cations showed resonances at δ = 5.944 ppm. and 5.922 ppm. respectively. Support for this conclusion comes from the observation that the experimental intensity ratio is that expected for a statistical

mixture of these four products.* Conversely, reaction of $RuBr_2(\eta^6\text{-}C_6H_6)py$ and $[RuCl(\eta^6\text{-}C_6H_6)(py)_2]PF_6$ (1:1 molar ratio) with HBF_4/MeOH gave a product analysing for $[Ru_2(\mu\text{-}Cl)(\mu\text{-}Br)_2(\eta^6\text{-}C_6H_6)_2]BF_4$ which showed the same four ^1H n.m.r. resonances as above but now with relative intensities 1:6:12:8 (Fig. 2.3b).

Fig. 2.3a and b.

Fourier transform ^1H n.m.r. spectra of the products of the reactions of $RuX_2(\eta^6\text{-}C_6H_6)py$ and $[RuX(\eta^6\text{-}C_6H_6)(py)_2]PF_6$ with HBF_4 in methanol.



*The statistical probability of forming the following cations starting from $RuCl_2(\eta^6\text{-}C_6H_6)py$ and $[RuBr(\eta^6\text{-}C_6H_6)(py)_2]PF_6$ (1:1 molar ratio) is as follows:-

$[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)_3Ru(\eta^6\text{-}C_6H_6)]^+$	2/3.2/3.2/3	=	8/27	= 8
$[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)_2(\mu\text{-}Br)(\eta^6\text{-}C_6H_6)]^+$	2/3.2/3.1/3 × 3	=	12/27	= 12
$[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)(\mu\text{-}Br)_2(\eta^6\text{-}C_6H_6)]^+$	2/3.1/3.1/3 × 3	=	6/27	= 6
$[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Br)_3Ru(\eta^6\text{-}C_6H_6)]^+$	1/3.1/3.1/3	=	1/27	= 1

The observation that the complexes "$\left[Ru_2(\mu\text{-}Cl)_2(\mu\text{-}Br)(\eta^6\text{-}C_6H_6)_2\right]BF_4$" and "$\left[Ru_2(\mu\text{-}Cl)(\mu\text{-}Br)_2(\eta^6\text{-}C_6H_6)_2\right]BF_4$" are in fact mixtures in solution, indicates that either the complexes are genuine single compounds in the solid state and rapidly rearrange when placed in solution, or that they are already a mixture of four triple halide bridged complexes. If the latter is true, then very facile halide exchange reactions must occur before and/or during and/or after the coupling process. Therefore, a number of further reactions were carried out in an attempt to clarify these interesting observations.

For example, it is readily demonstrated that facile halide exchange can occur prior to protonation since on mixing $\left[RuBr(\eta^6\text{-}C_6H_6)\text{-}py_2\right]PF_6$ and $RuCl_2(\eta^6\text{-}C_6H_6)PPh_3$* in $d^6\text{-}Me_2CO$ at ambient temperature and leaving for a few minutes, ^1H n.m.r. studies show that three new resonances at δ = 6.18 ppm., 5.47 ppm. and 5.45 ppm. are formed. These are readily assigned to the complexes $\left[RuCl(\eta^6\text{-}C_6H_6)(py)_2\right]PF_6$, $RuBr_2(\eta^6\text{-}C_6H_6)PPh_3$ and $RuBrCl(\eta^6\text{-}C_6H_6)PPh_3$ respectively. This was accompanied by a decrease in the intensity of the resonance due to $\left[RuBr(\eta^6\text{-}C_6H_6)(py)_2\right]PF_6$ (6.22 ppm.) and the complete disappearance of the resonance due to $RuCl_2(\eta^6\text{-}C_6H_6)PPh_3$ (5.43 ppm.) (Fig. 2.4(a) and (b)). Similar facile halide exchange processes were observed on mixing solutions of $\left[RuI(\eta^6\text{-}C_6H_3Me_3)py_2\right]PF_6$ and $RuCl_2(\eta^6\text{-}C_6H_3Me_3)py$, but surprisingly no halide exchange occurred between $\left[RuCl(\eta^6\text{-}C_6H_3Me_3)\text{-}py_2\right]PF_6$ and $RuI_2(\eta^6\text{-}C_6H_3Me_3)py$ under these conditions.

No halide exchange occurred when $\left[RuBr(\eta^6\text{-}C_6H_6)py_2\right]PF_6$ was shaken with an excess of LiCl in d^6-acetone at ambient temperature for several hours. However, when the reverse reaction was carried out ie. $\left[RuCl(\eta^6\text{-}C_6H_6)(py)_2\right]PF_6$ plus an excess of LiBr, complete

---

* The complex $RuCl_2(\eta^6\text{-}C_6H_6)PPh_3$ was used because of the insolubility of $RuCl_2(\eta^6\text{-}C_6H_6)py$ in acetone.

exchange readily occurred as shown by the disappearance of the n^6-C_6H_6 resonance at δ = 6.18 ppm. (chloro complex) and the appearance of a resonance at δ = 6.22 ppm. corresponding to the bromo complex.

Fig. 2.4a.

^{1}H n.m.r. spectra of $RuBr(n^6\text{-}C_6H_6)(py)_2PF_6$ and $RuCl_2(n^6\text{-}C_6H_6)PPh_3$ before mixing.

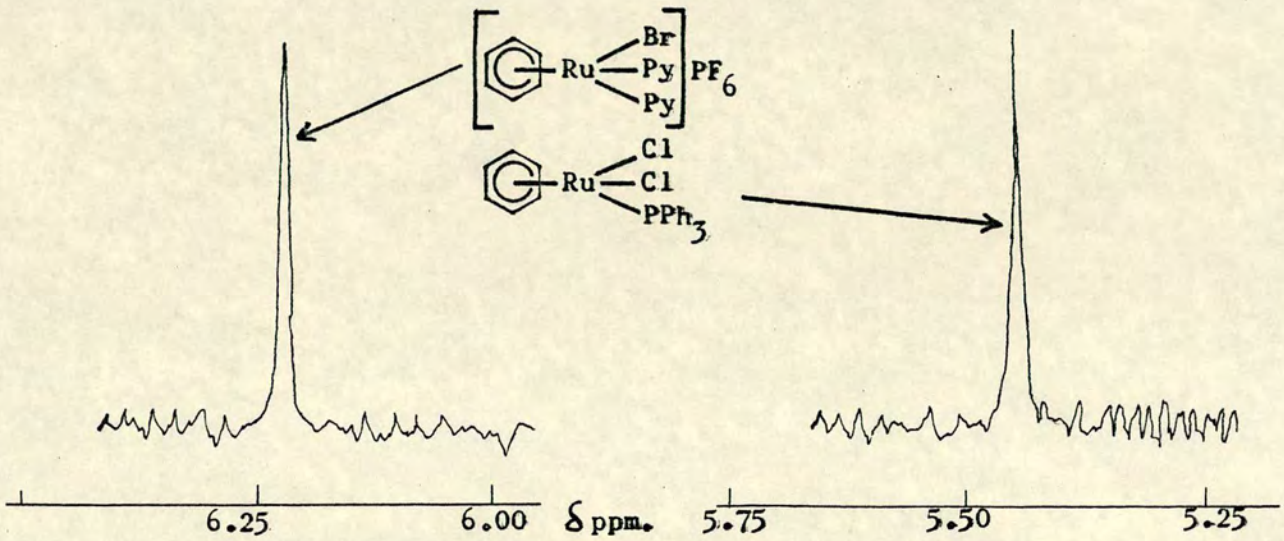
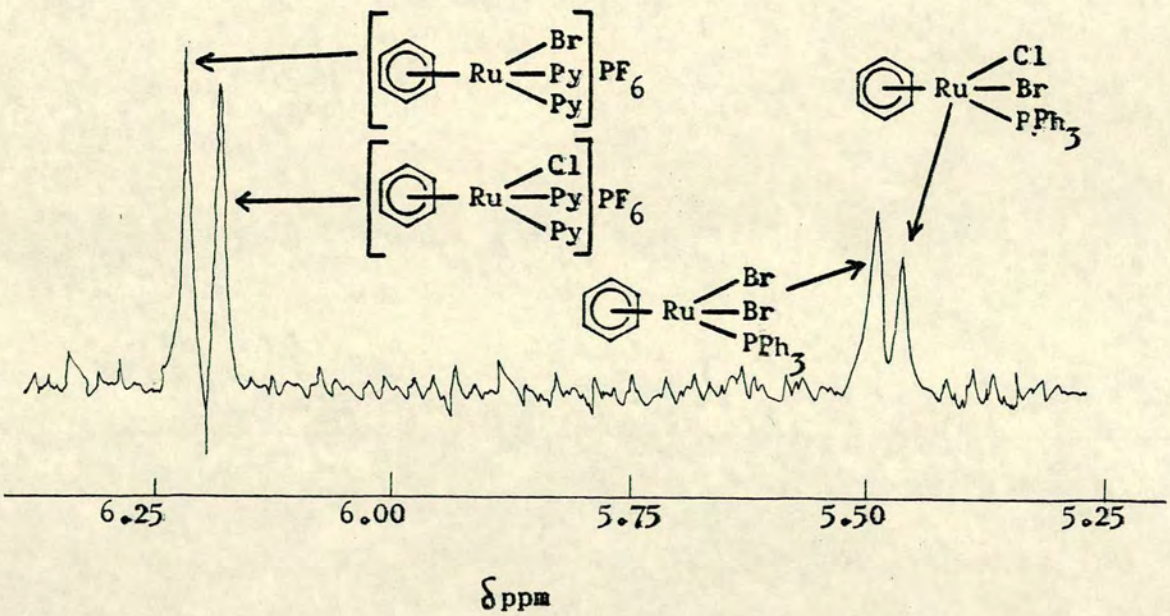


Fig. 2.4b.

^{1}H n.m.r. spectrum of above after mixing.

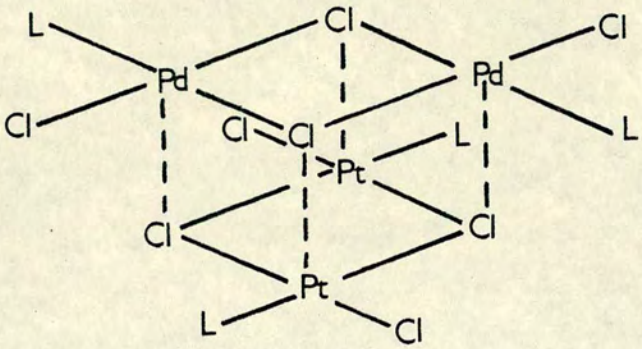


Hence, all these results would appear to indicate that the Ru-X bonds of the cationic complexes are more labile than those of the corresponding neutral monomers and, furthermore, that the order of displacement is $I^- > Br^- > Cl^-$.

It is interesting to note that $Mo_2(\mu\text{-}Cl)(\mu\text{-}Br)_2(\eta^7\text{-}C_7H_7)_2$ was apparently isolated as a pure mixed bridged complex by reaction of $MoBr(\eta^7\text{-}C_7H_7)(CO)_2$ with $SiMe_3Cl$ whereas the reverse reaction ie. $MoCl(\eta^7\text{-}C_7H_7)(CO)_2$ and $SiMe_3Br$ gave a product mixture (see Fig. 1.5, Chapter 1).[49,51] This is presumably a consequence of the heavier halogen preferring molybdenum and the lighter halogen preferring silicon. Furthermore, as discussed earlier (section 2.4), the synthesis of small amounts of $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2\right]BF_4$ by protonation of $\left[RuCl(\eta^6\text{-}C_6H_6)py_2\right]PF_6$ alone clearly indicates that facile chloride ion exchange occurs as a result of protonation (see Fig. 2.2). Therefore, irrespective of the halide attached to ruthenium in the $\left[RuX(\eta^6\text{-arene})py_2\right]^+$ cations, facile halide exchange will also occur on protonation, thus producing a complex mixture of solvated monomers (when the halide ions in the cationic and neutral monomers are, of course, different) which will then generate a statistical mixture of triple halide bridged compounds by cross-coupling reactions.

However, further complications are introduced by the observation that mixing $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2\right]BF_4$ and $\left[Ru_2(\mu\text{-}Br)_3(\eta^6\text{-}C_6H_6)_2\right]BF_4$ at ambient temperature in $d^3\text{-}MeNO_2$ and leaving for a few minutes produces a mixture of the $-(\mu\text{-}Cl)_3-$, $-(\mu\text{-}Cl)_2(\mu\text{-}Br)-$, $-(\mu\text{-}Cl)(\mu\text{-}Br)_2-$ and $-(\mu\text{-}Br)_3-$ cations (^1H n.m.r. evidence). In other words, facile halide exchange can also occur after the formation of the triple bridged cations. For this reason, no attempts have been made to separate the various species by either chromatographic or fractional crystallisation techniques.

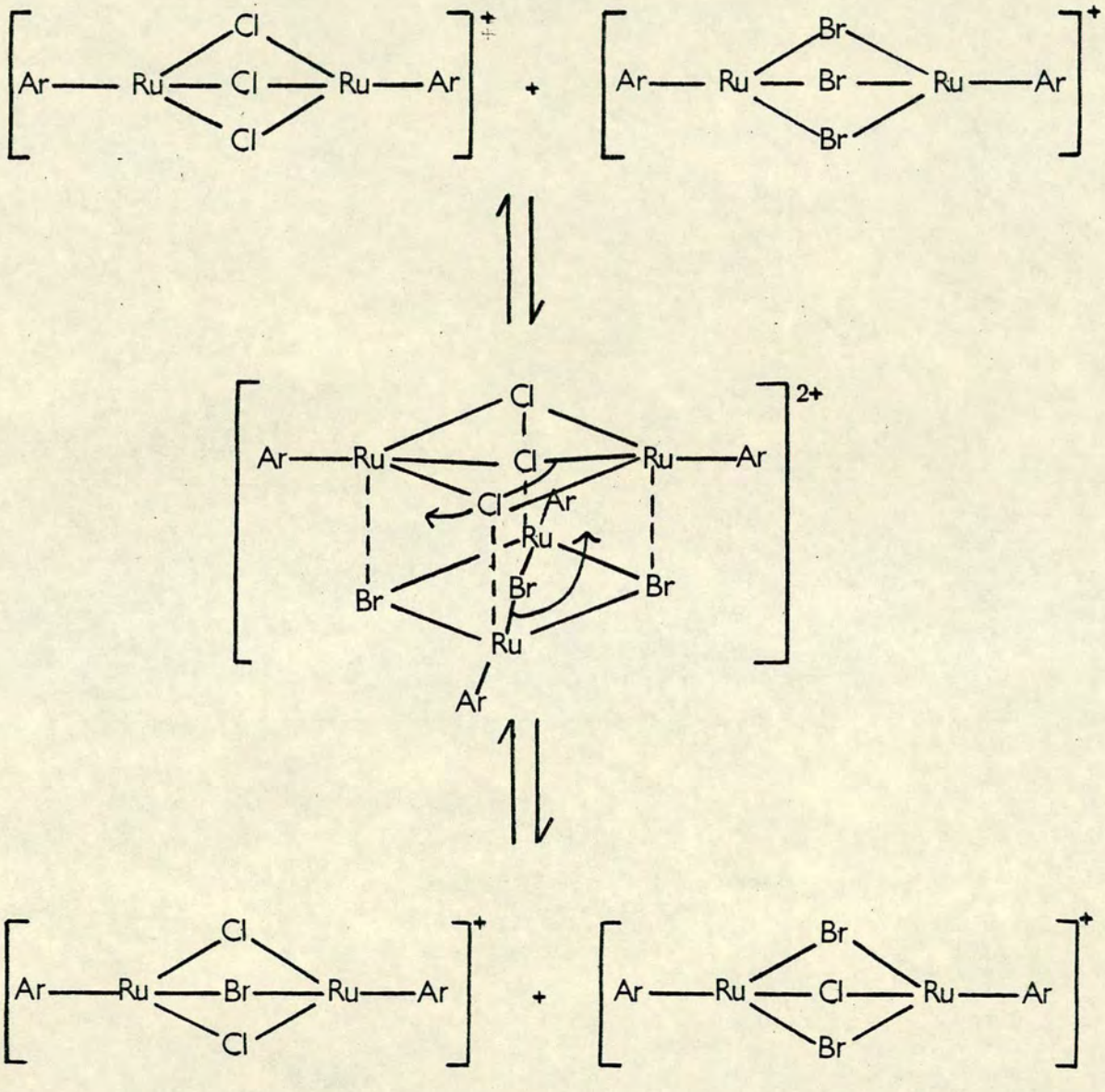
Possible mechanisms for this facile halide exchange reaction between the dimers are illustrated in Figures (2.5a) and 2.5b). A similar tetranuclear intermediate (64) to that in Fig. 2.5a has been postulated in the reaction of $Pd_2Cl_4L_2$ with $Pt_2Cl_4L_2$ to give some of the hetero-nuclear compound $PdPtCl_4L_2$ (L = PEt_3, P^nPr_3, P^nBu_3).[122]



(64)

Figs. 2.5a and 2.5b.

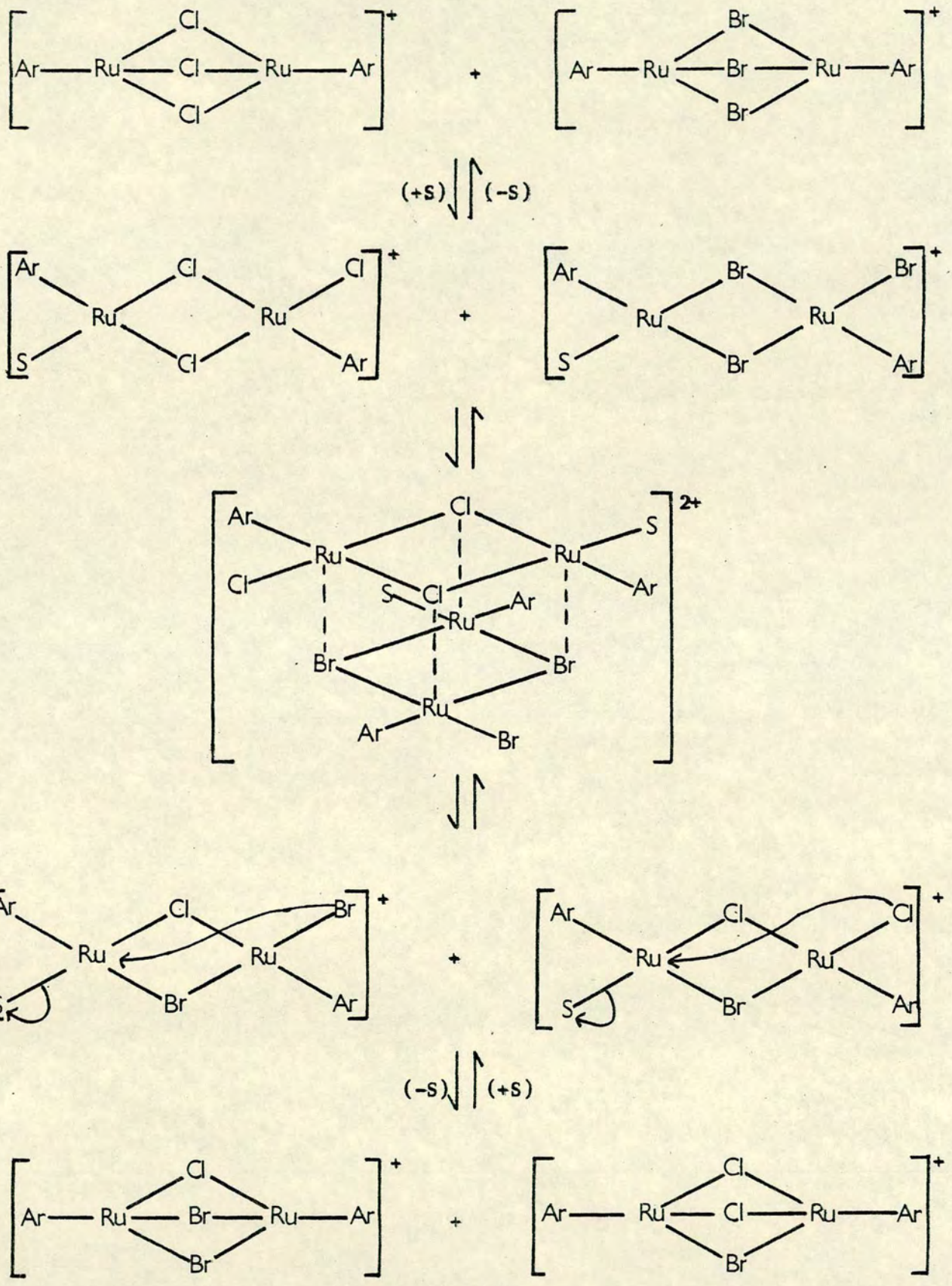
Possible mechanisms for halide exchange between the cations $[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2]^+$ and $[Ru_2(\mu\text{-}Br)_3(\eta^6\text{-}C_6H_6)_2]^+$.



$(Ar = \eta^6\text{-}C_6H_6)$

Alternatively the triple bridged complexes may undergo partial solvent assisted bridge cleavage to give double bridged cations of type (63) which could then exchange halogen as shown in Fig. 2.5b.

Fig. 2.5b.



(S = solvent; Ar = η^6-C_6H_6)

In an attempt to synthesise triple halide bridged heteroarene complexes an equimolar mixture of $RuCl_2(\eta^6\text{-}C_6H_6)py$ and $\left[RuCl(\eta^6\text{-}C_6H_3Me_3)(py)_2\right]PF_6$ was treated with HBF_4 in methanol. Although the product isolated, analysed quite well, for the mixed arene compound $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_3Me_3)\right]BF_4$, the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra in $d^3\text{-}MeNO_2$ showed that in solution this compound was a mixture of the three cations $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2\right]^+$, $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_3Me_3)_2\right]^+$ and $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_3Me_3)\right]^+$ (see Fig. 2.6a, b and Table 2.4).

Fig 2.6a.

^1H n.m.r. spectrum of the mixture produced by the reaction of $RuCl_2(\eta^6\text{-}C_6H_6)$ py and $\left[RuCl(\eta^6\text{-}C_6H_3Me_3)(py)_2\right]PF_6$ with HBF_4 in methanol.

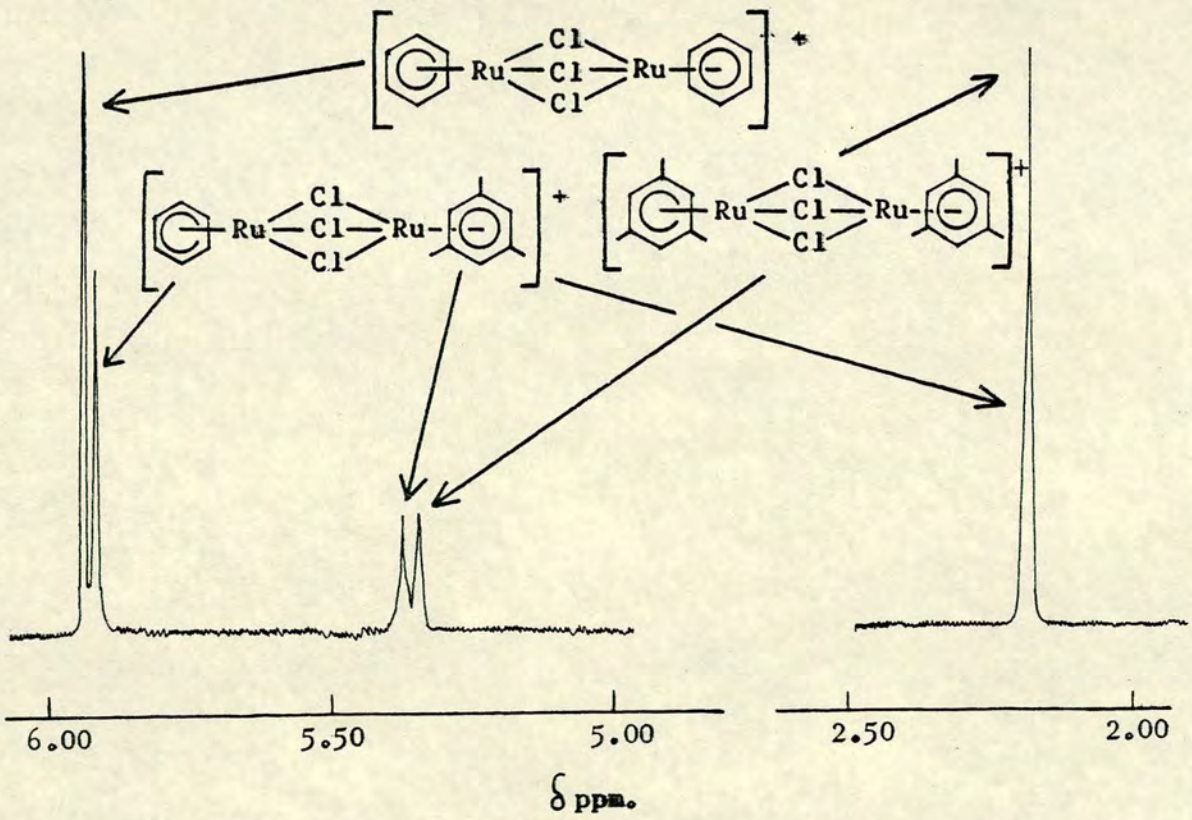
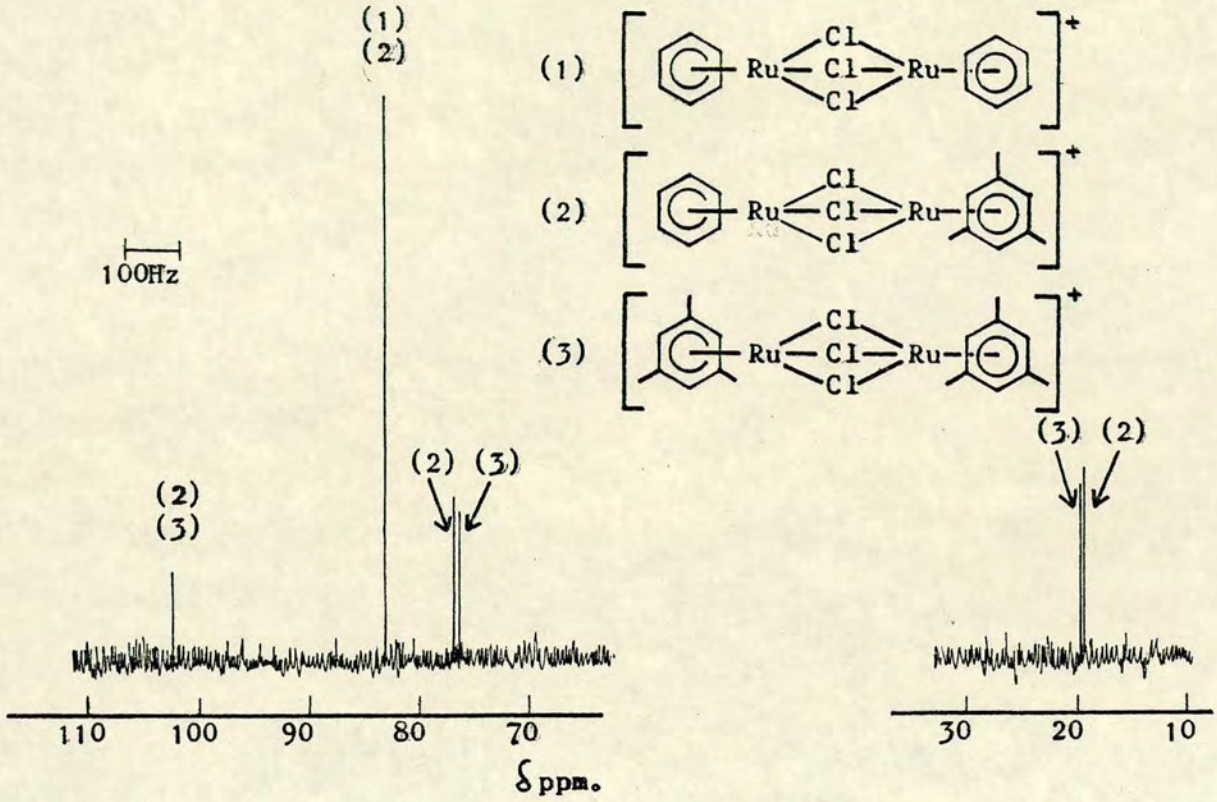


Fig. 2.6b.

$^{13}C-\{^{1}H\}$n.m.r. spectrum of the same mixture.



Similarly, reaction of $RuCl_2(\eta^6\text{-}C_6H_3Me_3)py$ and $\left[RuCl(\eta^6\text{-}C_6H_6)\text{-}(py)_2\right]PF_6$ with HBF_4/MeOH gave a product which analysed closely for the mixed arene compound, but ^1H and $^{13}C-\{^1H\}$ n.m.r. spectroscopy again showed that the same three cations are present in solution. Integration of the ^1H n.m.r. spectra of the products of these two reactions revealed that in the first case, the cations $\left[Ru_2(\mu\text{-}Cl)_3\text{-}(\eta^6\text{-}C_6H_6)_2\right]^+$, $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_3Me_3)_2\right]^+$ and $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)\text{-}(\eta^6\text{-}C_6H_3Me_3)\right]^+$ are present in the intensity ratio 2:1:2 and in the second 1:1·5:1 respectively. This suggests that on protonation, the monomers $RuCl_2(\eta^6\text{-arene})(py)$ must lose chloride ion and then couple to give the corresponding symmetric triple chloride bridged cations $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-arene})_2\right]^+$ more rapidly than the formation of

$RuCl_2(\eta^6\text{-arene})(solv)$, since in the first case, more bis-benzene than bis-mesitylene complex is formed whereas in the second reaction the opposite is found. When $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2\right]BF_4$ and $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_3Me_3)_2\right]BF_4$ are mixed in solution, ^1H n.m.r. studies reveal that in contrast to the $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2\right]^+ \left[Ru_2(\mu\text{-}Br)_3(\eta^6\text{-}C_6H_6)_2\right]^+$ system, the mixed arene cation is formed very slowly (several days). The comparative slowness of this scrambling process does not however, necessarily indicate that different mechanisms to those postulated earlier (Fig. 2.5) for halogen exchange are operating. The difference in rate may be due to unfavourable steric effects from the bulkier mesitylene rings which destabilises the proposed tetranuclear intermediates.

Attempts to synthesise the heteronuclear cations $\left[MM'(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)(\eta^5\text{-}C_5Me_5)\right]^+$ (M = Ru, M′ = Rh, Ir) by reaction of equimolar amounts of the complexes $\left[RuCl(\eta^6\text{-}C_6H_6)(py)_2\right]PF_6$ and $M'Cl_2(\eta^5\text{-}C_5Me_5)(py)$ with HBF_4/MeOH were unsuccessful since the only product isolated was $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2\right]BF_4$. This was obtained in good yield (based on ruthenium) indicating that on protonation, chloride ion had probably been preferentially abstracted from the M′ compounds to generate some $RuCl_2(\eta^6\text{-}C_6H_6)(solv.)$. Failure to isolate any $\left[M'_2(\mu\text{-}Cl)_3(\eta^5\text{-}C_5Me_5)_2\right]BF_4$ from this reaction is probably also due to the high solubility of the various $M'\text{-}\eta^5\text{-}C_5Me_5$ species which prevents their precipitation from solution. In contrast, the reaction of $RuCl_2(\eta^6\text{-}C_6H_6)py$ with $\left[OsCl(\eta^6\text{-}C_6H_6)(py)_2\right]PF_6$ and HBF_4 in MeOH gives an orange solid which analysed well (C,H,Cl) for the heteronuclear compound $\left[RuOs(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2\right]BF_4$. However, the ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra at 298K in $d^3\text{-}MeNO_2$ revealed that this product is a mixture of the complexes $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2\right]BF_4$, $\left[Os_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2\right]BF_4$ and $\left[RuOs(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2\right]BF_4$ (see Fig. 2.7 and Table 2.4).

Fig. 2.7a.

^{1}H n.m.r. spectrum in d^3-$MeNO_2$ at 298K of the mixture obtained from the reaction of $RuCl_2(\eta^6\text{-}C_6H_6)py$ and $[OsCl(\eta^6\text{-}C_6H_6)(py)_2]PF_6$ with HBF_4 in methanol.

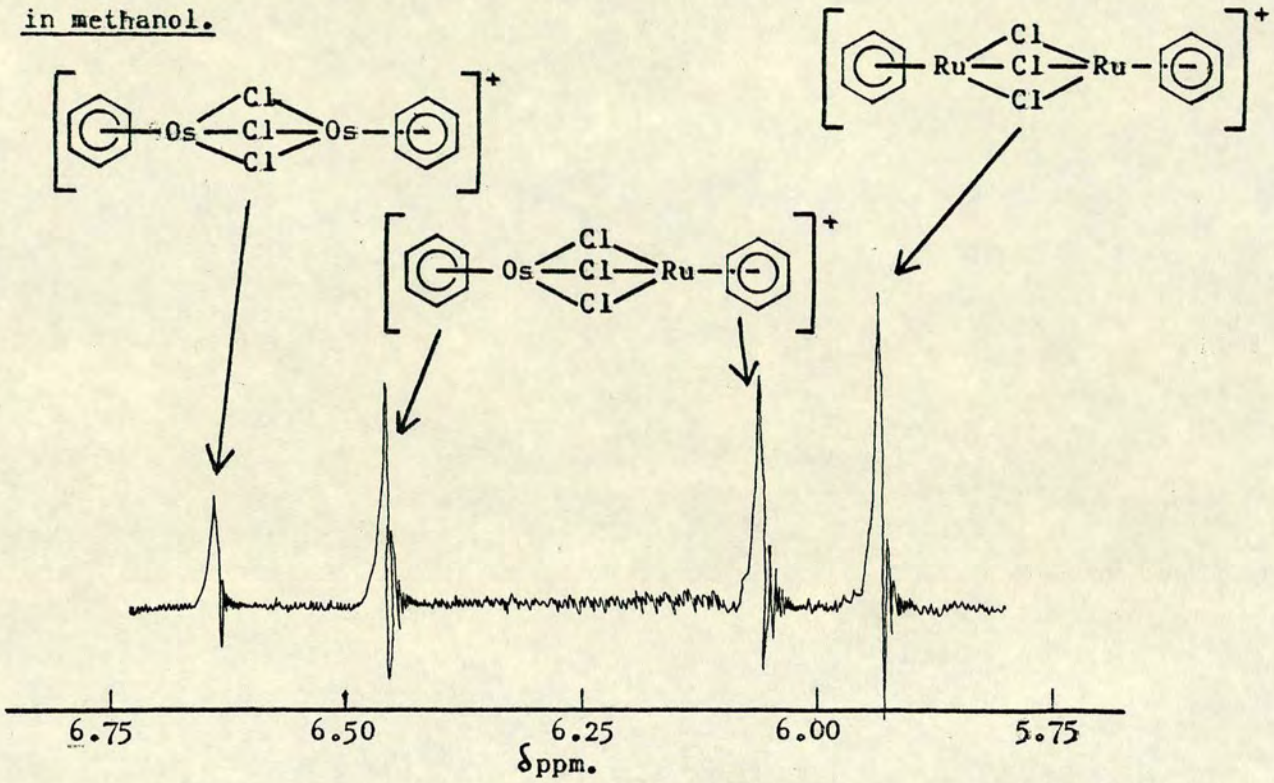
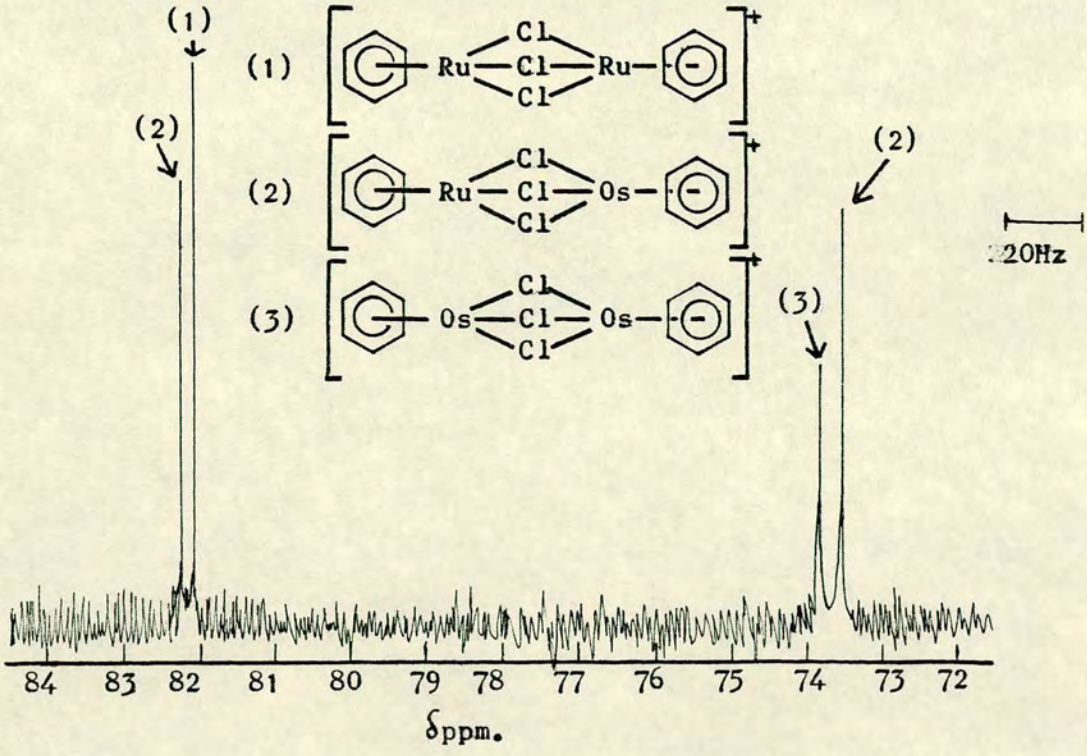


Fig. 2.7b.

$^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of the above mixture.

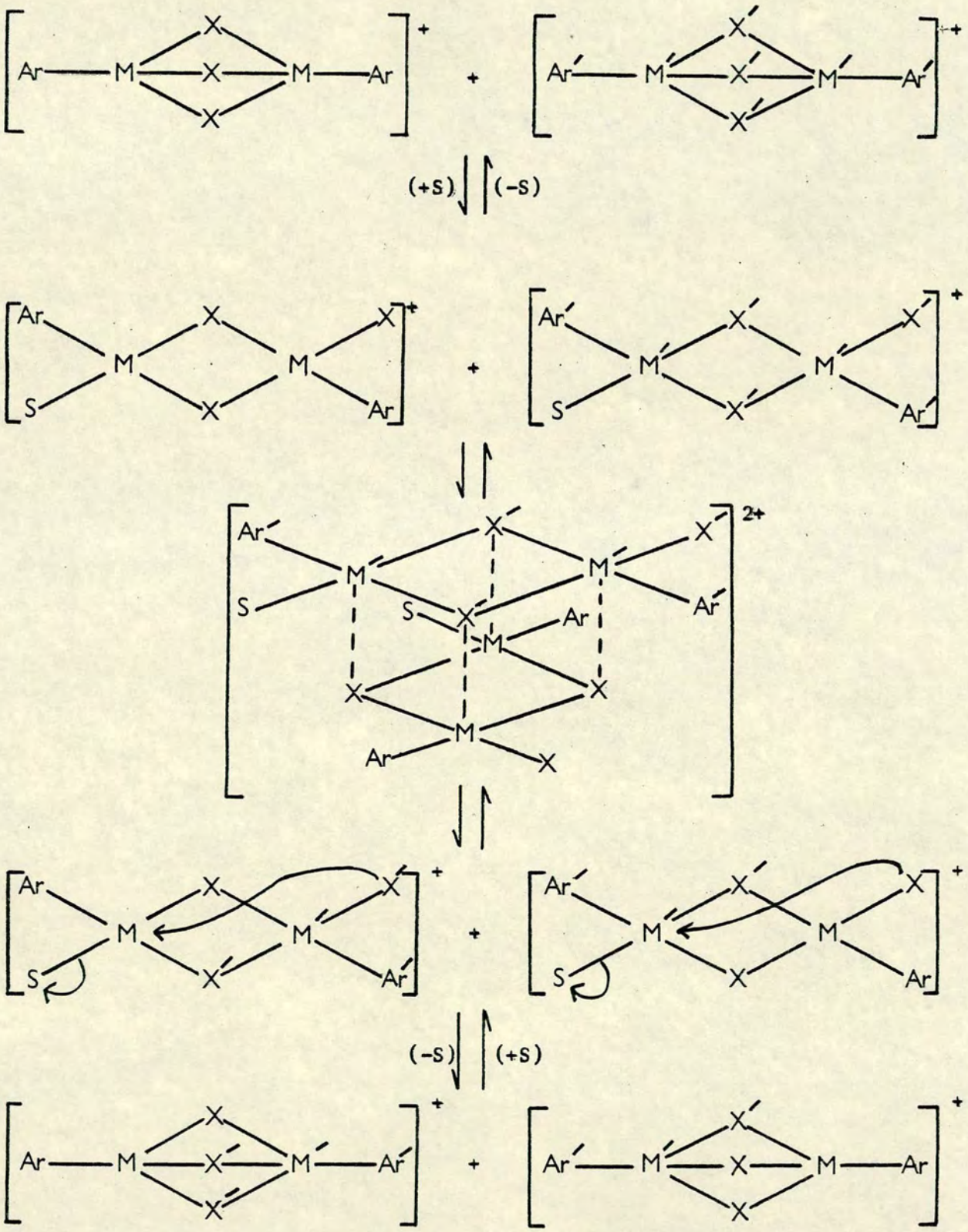


Rapid formation of this heteronuclear complex is found when solutions of $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2\right]BF_4$ and $\left[Os_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2\right]BF_4$ are mixed together although a pure sample of the mixed species could not be generated. A general reaction scheme for the formation of heterobridged, heteroarene, and heteronuclear complexes starting from the two cations $\left[M_2(\mu\text{-}X)_3(\eta^6\text{-arene})_2\right]^+$ and $\left[M'_2(\mu\text{-}X')_3(\eta^6\text{-arene}')_2\right]^+$ is outlined in Figure 2.8.

Finally, as shown in Table 2.4, the variations in the chemical shifts of both the aromatic protons and their associated carbons depend on the halide in the triple bridge and on the arene. Thus, when the arene is benzene, there is a decrease in the proton chemical shift as the bridging halide changes form chloride to bromide to iodide and this is accompanied by an increase in the chemical shift of the tertiary ring carbons. However, when the arene is mesitylene, there is an increase in the chemical shifts of the aromatic protons and a corresponding increase in the shift of the tertiary ring carbons, for the same change of halide. When the arene is p-cymene, there is no overall trend in the proton shift, but an increase in the carbon chemical shifts is observed. There are many different factors here which can influence the size and direction of n.m.r. chemical shifts eg. inductive and resonance effects of the halide, ring current effects, changes in configuration of the rings with respect to bridging groups etc. Since there is almost certainly a delicate balance between many of these factors, it is not feasible at this juncture to present a rationale for the observed trends.

Fig. 2.8.

Proposed general reaction scheme for the formation of heterobridged, heteroarene and heteronuclear cations.



(S = solvent; Ar = η^6-C_6H_6)

2.6 Conclusions.

A general route has been found for the syntheses of a variety of new triple halo bridged arene cations including some with different arenes, different metals and different bridging groups. However, because of facile scrambling processes before, during and after coupling of the monomeric precursors, pure samples of the latter could not be isolated. Nevertheless, much valuable spectroscopic information about these novel compounds has been discovered and quite detailed reaction schemes for the various scrambling processes have been inferred.

2.7 Experimental.

Microanalyses were by BMAC and the University of Edinburgh Chemistry Department. Infra-red spectra were recorded in the region 4000-250 cm^{-1} on a Perkin Elmer 457 grating spectrometer, using nujol mulls on caesium iodide plates. ^{1}H n.m.r. spectra were recorded on Varian Associates HA-100 and XL 100 (F.T.) spectrometers. $^{13}C-\{^{1}H\}$ spectra were recorded on a Jeol C.F. 20 spectrometer and ^{13}C chemical shifts are quoted in ppm. to high frequency of $SiMe_4$. Melting points were determined with a Kofler hot-stage microscope and are uncorrected. All reactions were carried out in degassed solvents under nitrogen. Analytical and n.m.r. data for the monomeric pyridine complexes are given in Tables 2.1 and 2.2 and for the triple halide bridged cations in Tables 2.3 and 2.4 respectively. Conductivity data were recorded on 10^{-3} mol dm^{-3} solutions in $MeNO_2$ on a Portland Electronics conductivity bridge at 298K. Molar conductance values (Λ_m) are quoted in $ohm^{-1}cm^{2}mol^{-1}$.

Starting Materials. The compounds $[RuCl_2(\eta^6\text{-arene})]_2$ (arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, p-$MeC_6H_4CH(Me)_2$, and C_6H_5OMe) were prepared by the following modifications of the literature methods.[47,115] Aqueous

solutions of the commercial ruthenium trichloride (pH 1.5) obtained from Johnson Matthey Ltd, were first evaporated to dryness several times on a water bath to remove most of the hydrochloric acid contaminant. This "purified $RuCl_3xH_2O$" was found to be much more reactive towards 1,3,- or 1,4- cyclohexadienes, since refluxing it in degassed 90% aqueous ethanol with cyclohexa-1,3-diene or cyclohexa-1,4-diene gave the complex $\left[RuCl_2(\eta^6\text{-}C_6H_6)\right]_2$ as a bright red solid after only 5-10 minutes. This is in marked contrast to the brown to red coloured solids isolated after three to four hours at 40°C with "unpurified" ruthenium trichloride. The red $\left[RuCl_2(\eta^6\text{-}C_6H_6)\right]_2$ is much more reactive than the previously isolated brown compound, which is believed to be polymeric, rather than dimeric in nature. The reaction times with other cyclohexadienes eg. 1-methoxycyclohexa-1,4-diene or α-phellandrene (5-isopropyl-2-methylcyclohexa-1,3-diene), were also greatly reduced from those quoted elsewhere.[47] However, the reaction with 1,3,5-trimethylcyclohexa-1,4-diene took 16 hours for completion, as reported.[47]

The complexes $\left[RuX_2(\eta^6\text{-arene})\right]_2$ ($X = Br^-$, I^-, SCN^-, arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, p-$MeC_6H_4CH(Me)_2$ were prepared by the addition of LiX to saturated solutions of the corresponding chloro compounds in water.

The complexes $\left[OsCl_2(\eta^6\text{-arene})\right]_2$ (arene = C_6H_6, p-$MeC_6H_4CH(Me)_2$) were prepared in low yields (ca 30%) by the reaction of the appropriate cyclohexadiene (10 cm^3) with Na_2OsCl_6 (1.00g) in a minimum amount (10 cm^3) of commercial ethanol. They were isolated as yellow solids after refluxing for several hours. The reaction of cyclohexa-1,3-diene with $OsCl_3$ has been reported[124a] to give $\left[OsCl_2(\eta^6\text{-}C_6H_6)\right]_2$ in 65% yield.

The compounds 1,3,5-trimethylcylohexa-1,4,diene,1-methoxycyclohexa 1,4-diene and cyclohexa-1,4-diene were prepared by the standard Birch reduction of the corresponding arenes.[123]

The complexes $[MX_2(\eta^5\text{-}C_5Me_5)]_2$ and $MX_2(\eta^5\text{-}C_5Me_5)py$ (M = Rh, Ir; X = Cl^-, I^-) were prepared by standard literature methods.[124b]

The compounds $[RuCl(\eta^6\text{-}C_6H_6)(N\text{-}N)]PF_6$ (N-N) = 2,2′-bipyridyl or 1,10-phenanthroline and the isolectronic $[M'Cl(\eta^5\text{-}C_5Me_5)(N\text{-}N)]PF_6$ (M′ = Rh or Ir) were prepared by similar routes (see refs. 113 and 116).

Chemicals: Ruthenium trichloride hydrate and sodium hexachloro osmate (IV) (Johnson-Matthey Ltd) ∝-phellandrene (Eastman Chemicals); d^3-$MeNO_2$ and cyclohexa-1,3-diene (Aldrich Chemicals); LiBr, LiI, LiSCN (BDH); pyridine and HBF_4 (40% aqueous solution) (Fisons); ammonium hexafluorophosphate and $AgPF_6$ (Alfa products).

Synthesis of the pyridine monomers.

(η^6-benzene)dichloro(pyridine)ruthenium(II).

The compound $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ (0.20g, 0.40 mmol) was shaken with pyridine (10 cm^3) for several days, to give an orange solid. This was filtered and washed with methanol and diethylether. Yield 65%; m.p. 245°C (decomp); ν(Ru-Cl), 280 cm^{-1}; ν(C = N), 1600 cm^{-1}; ν(C=C), 825 cm^{-1}.

The complexes:-(η^6-benzene)dibromo(pyridine)ruthenium(II) yield 67%; ν(C=N), 1600 cm^{-1}; ν(C=C),825 cm^{-1}; (η^6-mesitylene)dichloro(pyridine) ruthenium(II) yield 37%; m.p. 210°C(decomp); ν(C=N),595 cm^{-1}; ν(Ru-Cl), 277 cm^{-1}; (η^6-mesitylene)di(iodo)(pyridine)ruthenium(II) yield 56%; m.p. 120°C(decomp); ν(C=N),1600 cm^{-1} were prepared similarly.

(η^6-benzene)chloro bis(pyridine)ruthenium(II)hexafluorophosphate

Method A. The compound $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ (0.20g, 0.40 mmol) was stirred in methanol (10 cm^3) with pyridine (0.20 cm^3) to give a yellow

solution. This was filtered and a solution of excess NH_4PF_6 in methanol (5 cm^3) was added to give a copious yellow precipitate. This was filtered, washed with water, methanol and finally diethyl ether. Yield 82%; m.p. 227°C(decomp); ν(Ru-Cl),280 cm^{-1}, ν(C=N), 1602 cm^{-1}; Λ_m = 84.[113]

Method B. The filtrate from the reaction of the compound $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ with neat pyridine was concentrated and the residue dissolved in methanol. Addition of NH_4PF_6 as in method A gave the compound $[RuCl(\eta^6\text{-}C_6H_6)(py)_2]PF_6$ in 10% yield.

(η^6-benzene)bromobis(pyridine)ruthenium(II)hexafluorophosphate.

The compound $[RuBr_2(\eta^6\text{-}C_6H_6)]_2$ (0.20g) was refluxed in methanol/pyridine (1:1 v/v) (10 cm^3) for four hours. The orange solution was filtered to remove undissolved starting compound and then excess NH_4PF_6 was added to give an orange precipitate. This was filtered and washed as for the corresponding chloro complex. Yield 50%; ν(C=N), 1610 cm^{-1}; Λ_m = 78.

The following compounds were synthesised via methods A and B.

(η^6-mesitylene)chlorobis(pyridine)ruthenium(II)hexafluorophosphate.

Method A. Yield 45%; Method B. Yield 61%; m.p. 220°C(decomp); ν(Ru-Cl),295 cm^{-1}, ν(C=N),1605 cm^{-1}; Λ_m = 71.

(η^6-mesitylene)bromobis(pyridine)ruthenium(II)hexafluorophosphate.

Method A. Yield 71%; Method B. Yield 10%; m.p. 222°C(decomp); ν(C=N), 1610 cm^{-1}; Λ_m = 78.

(η^6-mesitylene)iodobis(pyridine)ruthenium(II)hexafluorophosphate.

Method A. Yield 54%; Method B. Yield 14%; m.p. 220°C(decomp); ν(C=N), 1600 cm^{-1}.

(η^6-p-cymene)chlorobis(pyridine)ruthenium(II)hexafluorophosphate.

The compound $[RuCl_2(\eta^6\text{-p-cymene})]_2$ (0.10g) was shaken in pyridine (10 cm^3) to give an orange solution, which was then concentrated to dryness. The residue was extracted with methanol to give an

orange solid (impure $RuCl_2(\eta^6\text{-p-cymene})py$) and an orange solution. Excess NH_4PF_6 was added to the solution which was then taken to dryness. The yellow residue was shaken with water and the yellow precipitate filtered off, washed with diethyl ether and dried in vacuo. Yield 41%; ν(Ru-Cl),280 cm^{-1}; ν(C=N),1595 cm^{-1}.

(η^6-benzene)chlorobis(pyridine)osmium(II)hexafluorophosphate.

The compound $\left[OsCl_2(\eta^6\text{-}C_6H_6)\right]_2$ (0.10g) was refluxed in ethanol/pyridine (1:1 v/v) (20 cm^3) until a yellow solution had formed (2-3 hrs). This was then filtered and excess NH_4PF_6 in methanol added. The solution was taken to dryness and the residue redissolved in methanol (5 cm^2) and on standing a yellow precipitate formed. This was filtered and washed with water and diethylether. Yield 90%; m.p. 225-227°C; ν(Os-Cl),285 cm^{-1}; ν(C=N),1605 cm^{-1}.

(η^6-p-cymene)chlorobis(pyridine)osmium(II)hexafluorophosphate.

The compound $\left[OsCl_2(\eta^6\text{-p-cymene})\right]_2$ (0.16g, 0.20 mmol) was stirred in methanol (10 cm^3) with pyridine (0.20 cm^3) to give a yellow solution. Excess NH_4PF_6 in methanol was added and the solution taken to dryness. The residue was extracted with acetone and filtered; concentration of the filtrate gave a yellow solid which was filtered and washed with water and diethylether. Yield 32%; m.p. 175-177°C; ν(Os-Cl),290 cm^{-1}; ν(C=N),1610 cm^{-1}.

(η^5-pentamethylcyclopentadienyl)chlorobis(pyridine)iridium(III). hexafluorophosphate.

By method A from $\left[IrCl_2(\eta^5\text{-}C_5Me_5)\right]_2$. Yield 83%.

Synthesis of triple halide bridged, binuclear complexes.

Tri-μ-chlorobis[(η^6-benzene)ruthenium(II)]tetrafluoroborate.

Method A. The compounds $RuCl_2(\eta^6\text{-}C_6H_6)py$(0.10 mmol) and $\left[RuCl(\eta^6\text{-}C_6H_6)(py)_2\right]PF_6$ (0.10 mmol) were suspended in methanol (10 cm^3). Tetrafluoroboric acid (HBF_4, 40% sol.), (1 cm^3) was added and the

solution stirred vigorously. The suspended solids immediately dissolved to give an orange solution, from which an orange, microcrystalline solid was rapidly precipitated. The mixture was gently warmed for 1 hour and the solid was then filtered off. Concentration of the filtrate gave more of the orange compound. The solid was washed with methanol and diethylether. Yield 92%; m.p. 270°C(decomp); ν(Ru-Cl), 260 cm^{-1}; Λ_m = 76.

Method B. The compound $\left[RuCl(\eta^6\text{-}C_6H_6)(py)_2\right]PF_6$ (0.30 mmol) was suspended in methanol (10 cm^3) and HBF_4 (1.0 cm^3) was added as above. An orange solid was formed and isolated as for method A. This complex was identical to that formed by method A. Yield 82%, (based on chloride), 27%, (based on Ru).

Tri-μ-bromobis[η^6-benzene)ruthenium(II)]tetrafluoroborate.

This complex was synthesised by method A using the compounds $RuBr_2(\eta^6\text{-}C_6H_6)py$ and $\left[RuBr(\eta^6\text{-}C_6H_6)(py)_2\right]PF_6$. Yield 87%; m.p. 270°C (decomp); Λ_m = 82.

Tri-μ-chlorobis[(η^6-mesitylene)ruthenium(II)]tetrafluoroborate.

From method A. Yield 86%; m.p. 280°C(decomp); ν(Ru-Cl),260 cm^{-1} Λ_m = 77.

Tri-μ-bromobis[(η^6-mesitylene)ruthenium(II)]tetrafluoroborate.

By method B using $\left[RuBr(\eta^6\text{-}C_6H_3Me_3)(py)_2\right]PF_6$. Yield 53%, (based on bromide); 18% (based on Ru); Λ_m = 79.

Tri-μ-iodobis[(η^6-mesitylene)ruthenium(II)]tetrafluoroborate.

By method A. Yield 71%; m.p. 260°C(decomp); Λ_m = 88.

Tri-μ-chlorobis[(η^6-benzene)osmium(II)]tetrafluoroborate.

By method B using $\left[OsCl(\eta^6\text{-}C_6H_6)(py)_2\right]PF_6$. Yield 83%,(based on chloride), 28%,(based on Os).

Tri-μ-bromobis[(η^6-benzene)ruthenium(II)]hexafluorophosphate.

The compound $\left[RuBr_2(\eta^6\text{-}C_6H_6)\right]_2$ (0.20 mmol) was suspended in

nitromethane (10 cm^3) with $AgPF_6$ (0.20 mmol). The mixture was stirred for several hours and the AgBr precipitate was filtered off through celite. The filtrate was taken to dryness and the residue washed with methanol to give an orange solid, which was filtered off and washed with diethylether. Yield 34%; m.p. 276°C(decomp); Λ_m = 77. The following complexes were prepared similarly.

Tri-μ-iodobis[η^6-benzene)ruthenium(II)]hexafluorophosphate. Yield 32%.

Tri-μ-chlorobis[(η^6-p-cymene)ruthenium(II)]hexafluorophosphate (in acetone). Yield 58%; m.p. 197°-199°C; ν(Ru-Cl),260 cm^{-1}.

Tri-μ-bromobis[(η^6-p-cymene)ruthenium(II)]hexafluorophosphate (in acetone) Yield 85%; m.p. 250-252°C; Λ_m = 77. Tri-μ-iodobis[(η^6-p-cymene) ruthenium(II)]hexafluorophosphate (in acetone). Yield 54%; m.p. 265°C (decomp); Λ_m = 74.

The following complexes were synthesised by method A although as discussed in detail earlier (see section 2.5), facile exchange processes led to product mixtures.

"μ-bromo-di-μ-chlorobis[(η^6-benzene)ruthenium(II)]tetrafluoroborate"

From the compounds $RuCl_2(\eta^6\text{-}C_6H_6)py$ and $\left[RuBr(\eta^6\text{-}C_6H_6)(py)_2\right]PF_6$ Yield 87%; Λ_m = 79.

"Di-μ-bromo-μ-chlorobis[(η^6-benzene)ruthenium(II)]tetrafluoroborate"

From the compounds $RuBr_2(\eta^6\text{-}C_6H_6)py$ and $\left[RuCl(\eta^6\text{-}C_6H_6)(py)_2\right]PF_6$. Yield 88%; Λ_m = 74.

"Tri-μ-chloro(η^6-benzene)osmium(II)(η^6-benzene)ruthenium(II)tetrafluoroborate"

From the compounds $RuCl_2(\eta^6\text{-}C_6H_6)py$ and $\left[OsCl(\eta^6\text{-}C_6H_6)(py)_2\right]PF_6$ Yield 70%.

"Tri-μ-chloro(η^6-benzene)(η^6-mesitylene)ruthenium(II)tetrafluoroborate"

From the compounds $RuCl_2(\eta^6\text{-}C_6H_6)py$ and $\left[RuCl(\eta^6\text{-}C_6H_3Me_3)(py)_2\right]PF_6$ or $RuCl_2(\eta^6\text{-}C_6H_3Me_3)py$ and $\left[RuCl(\eta^6\text{-}C_6H_6)(py)_2\right]PF_6$. Yields 86% and 73% respectively; ν(Ru-Cl),260 cm^{-1}; Λ_m = 78 for both products.

Table 2.1.

Analytical data on some monomeric pyridine complexes.

Compound	Found(%)			Calculated(%)		
	C	H	N	C	H	N
$RuCl_2(\eta^6\text{-}C_6H_6)py$	40.2	3.4	4.3	40.1	3.4	4.3
$RuBr_2(\eta^6\text{-}C_6H_6)py$	31.9	2.7	3.2	31.6	2.7	3.4
$RuCl_2(\eta^6\text{-}C_6H_3Me_3)py$	45.3	4.6	3.8	45.3	4.6	3.8
$[RuCl(\eta^6\text{-}C_6H_6)(py)_2]PF_6$	36.9	3.0	5.4	37.1	3.1	5.4
$[RuBr(\eta^6\text{-}C_6H_6)(py)_2]PF_6$	34.2	2.8	4.9	34.2	2.9	5.0
$[RuCl(\eta^6\text{-}C_6H_3Me_3)(py)_2]PF_6$	40.6	3.9	4.9	40.8	4.0	5.0
$[RuBr(\eta^6\text{-}C_6H_3Me_3)(py)_2]PF_6$	37.3	3.7	5.3	37.8	3.7	4.6
$[RuI(\eta^6\text{-}C_6H_3Me_3)(py)_2]PF_6$	34.8	3.4	4.5	35.0	3.4	4.3
$[RuCl(\eta^6\text{-p-cymene})(py)_2]PF_6$	41.6	4.1	4.8	41.9	4.2	4.9
$[OsCl(\eta^6\text{-}C_6H_6)(py)_2]PF_6$	31.8	2.7	4.7	31.7	2.7	4.6
$[OsCl(\eta^6\text{-p-cymene})(py)_2]PF_6$	36.2	3.6	4.3	36.2	3.7	4.2
$[IrCl(\eta^5\text{-}C_5Me_5)(py)_2]PF_6$	36.0	3.8	4.1	36.1	3.8	4.2

Table 2.2.

^{1}H n.m.r. data for some neutral and cationic pyridine monomeric complexes[a]

δ ppm.[b]

Compound	Ring Protons	Other Resonances	Pyridine Resonances
$RuCl_2(\eta^6\text{-}C_6H_3Me_3)py$	4.88(s),[3H].	2.02(s),[9H,Me].	9.02(m),7.69(m),7.29(m),[5H].
$RuBr_2(\eta^6\text{-}C_6H_3Me_3)py$[c]	4.96(s),[3H].	2.15(s),[9H,Me].	----------
$RuI_2(\eta^6\text{-}C_6H_3Me_3)py$	5.10(s),[3H].	2.25(s),[9H,Me].	9.40(m),7.70(m),7.25(m),[5H].
$RuCl_2(\eta^6\text{-p-cymene})py$[c]	5.30(AB),[4H].	2.98(se),[1H,C<u>H</u>(Me)$_2$];2.08(s),[3H,p-Me];1.28(d),[6H,CH(<u>Me</u>)$_2$][d].	----------
$[RuCl(\eta^6\text{-}C_6H_6)(py)_2]PF_6$	6.17(s),[6H].	-------	8.85(m),8.00(m),7.45(m),[10H].
$[RuBr(\eta^6\text{-}C_6H_6)(py)_2]PF_6$	6.22(s),[6H].	-------	8.85(m),8.04(m),7.48(m),[10H].
$[RuCl(\eta^6\text{-}C_6H_3Me_3)(py)_2]PF_6$	5.49(s),[3H].	1.96(s),[9H,Me].	9.18(m),8.06(m),7.58(m),[10H].
$[RuBr(\eta^6\text{-}C_6H_3Me_3)(py)_2]PF_6$	5.57(s),[3H].	2.03(s),[9H,Me].	9.16(m),8.06(m),7.59(m),[10H].
$[RuI(\eta^6\text{-}C_6H_3Me_3)(py)_2]PF_6$	5.69(s),[3H].	2.15(s),[9H,Me].	9.10(m),8.10(m),7.60(m),[10H].
$[RuCl(\eta^6\text{-p-cymene})(py)_2]PF_6$	5.72(AB),[4H].	2.66(se),[1H,C<u>H</u>(Me)$_2$];1.73(s),[3H,p-Me];1.13(d),[6H,CH(<u>Me</u>)$_2$][d]	8.88(m),7.85(m),7.42(m),[10H].
$[OsCl(\eta^6\text{-}C_6H_6)(py)_2]PF_6$	6.38(s),[6H].	-------	8.93(m),8.10(m),7.50(m),[10H].

Table 2.2 (cont).

Compound	Ring Protons	Other resonances	Pyridine resonances
$[OsCl(\eta^6\text{-p-cymene})(py)_2]PF_6$	6.23(AB),[4H].	2.74(se),[1H,C<u>H</u>(Me)$_2$];1.82(s),[3H,p-Me];1.18(d),[6H,CH(<u>Me</u>)$_2$][d]	8.90(m),8.02(m),7.48(m),[10H].
$[IrCl(\eta^5\text{-}C_5Me_5)(py)_2]PF_6$	------	1.55(s),[15H,Me].	8.99(m),8.09(m),7.64(m),[10H].

s = singlet, d = doublet, se = septet, m = multiplet. [a] All neutral complexes recorded in $CDCl_3$ and cationic complexes in d^6-Me_2CO at 298K. [b] Reference is $SiMe_4$ (internal lock). [c] N.m.r. parameters of these compounds obtained from mixtures and therefore no pyridine resonances are quoted. [d] $^3J(HH)$ for (d) and (se) of p-cymene complexes was about 6Hz in all cases.

Table 2.3.

Analytical data for some triple halide bridged complexes.

Compound	Found(%)			Calculated(%)		
	C	H	Halide	C	H	Halide
$[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2]BF_4$	26.0,	2.1,	18.6(Cl)	26.1,	2.2,	19.3(Cl)
$[Ru_2(\mu\text{-}Br)_3(\eta^6\text{-}C_6H_6)_2]BF_4$	21.3,	1.9,	32.7(Br)	21.0,	1.8,	35.0(Br)
$[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2]PF_6$	23.8,	2.0,	--	23.6,	2.0,	--
$[Ru_2(\mu\text{-}Br)_3(\eta^6\text{-}C_6H_6)_2]PF_6$	19.4,	1.6,	--	19.4,	1.6,	--
$[Ru_2(\mu\text{-}I)_3(\eta^6\text{-}C_6H_6)_2\ PF_6$	16.3,	1.3,	--	16.3,	1.4,	--
$"[Ru_2(\mu\text{-}Br)(\mu\text{-}Cl)_2(\eta^6\text{-}C_6H_6)_2]BF_4"$	24.2,	2.0,	12.1(Cl),13.9(Br)	24.2,	2.0,	11.9(Cl),13.4(Br).
$"[Ru_2(\mu\text{-}Br)_2(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)_2]BF_4"$	22.6,	1.9,	5.5(Cl),24.7(Br)	22.5,	1.94,	5.5(Cl),24.9(Br).
$[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_3Me_3)_2]BF_4$	33.8,	3.5,	--	34.0,	3.8,	--
$[Ru_2(\mu\text{-}Br)_3(\eta^6\text{-}C_6H_3Me_3)_2]BF_4$	27.9,	3.0,	--	28.1,	3.2,	--
$[Ru_2(\mu\text{-}I)_3(\eta^6\text{-}C_6H_3Me_3)_2]BF_4$	23.5,	2.6,	41.6(I)	23.8,	2.7,	41.8(I)
$"[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_3Me_3)]BF_4{}^a"$	29.4,	2.9,	--	30.3,	3.0,	--
$[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}p\text{-cymene})_2]PF_6$	33.3,	4.0,	--	33.3,	3.9,	--
$[Ru_2(\mu\text{-}Br)_3(\eta^6\text{-}p\text{-cymene})_2]PF_6$	27.9,	3.2,	--	28.1,	3.3,	--

Table 2.3 cont.

Compound	Found(%)			Calculated(%)		
	C	H	Halide	C	H	Halide
$[Ru_2(\mu\text{-}I)_3(\eta^6\text{-}p\text{-cymene})_2]PF_6$	24.8,	2.8,	38.0(I)	24.1,	2.8,	38.2(I)
$[Os_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2]BF_4$	21.5,	2.0,	--	21.3,	1.8,	--
" $[OsRu(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2]BF_4$ "	22.5,	1.8,	16.8(Cl)	22.5,	1.9,	16.6(Cl).

(a) Compound from $RuCl_2\eta^6\text{-}C_6H_6py$ + $[RuCl_3\eta^6\text{-}C_6H_3Me_3(py)_2]PF_6$

Table 2.4.

^{1}H and $^{13}C-\{^{1}H\}$ n.m.r. spectra of some binuclear complexes in d^{3}-$MeNO_2$ at 298K.

Compound	^{1}H n.m.r. δppm	$^{13}C-\{^{1}H\}$ n.m.r. δppm
$[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2]BF_4$	5.945(s)[a], (5.93(s)[b]).	82.0.
$[Ru_2(\mu\text{-}Br)_3(\eta^6\text{-}C_6H_6)_2]BF_4$	5.924(s)[a].	82.4.
$[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2]PF_6$	5.93(s)[b].	82.0.
$[Ru_2(\mu\text{-}Br)_3(\eta^6\text{-}C_6H_6)_2]PF_6$	5.92(s)[b]	82.3.
$[Ru_2(\mu\text{-}I)_3(\eta^6\text{-}C_6H_6)_2]PF_6$	5.88(s)[b].	83.3.
$[Ru_2(\mu\text{-}Br)(\mu\text{-}Cl)_2(\eta^6\text{-}C_6H_6)_2]BF_4$[c]	5.937(s)[a].	82.2.
$[Ru_2(\mu\text{-}Br)_2(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)_2]BF_4$[c]	5.929(s)[a].	82.3.
$[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_3Me_3)_2]BF_4$	5.35(s),[6H];2.22(s),[18H,Me].	102.0(A);75.7(B);19.4(C).
$[Ru_2(\mu\text{-}Br)_3(\eta^6\text{-}C_6H_3Me_3)_2]BF_4$	5.38(s),[6H];2.23(s),[18H,Me].	100.3(A);77.6(B);19.9(C).
$[Ru_2(\mu\text{-}I)_3(\eta^6\text{-}C_6H_3Me_3)_2]BF_4$	5.52(s),[6H];2.30(s),[18H,Me].	97.6(A);81.7(B);20.7(C).
$[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_6H_3Me_3)]BF_4$[c]	5.92(s),[6H];5.37(s),[3H]; 2.22(s),[9H,Me].	102.0(A);82.0;75.9(B);19.3(C).

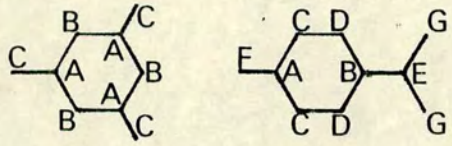
Table 2.4 cont.

Compound	^{1}H n.m.r.	^{13}C n.m.r.
$[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-p-cymene})_2]PF_6$	5.70(AB), [8H,C_6H_4];2.84(se) [2H,C<u>H</u>(Me)$_2$];2.23(s), [6H,p-Me];1.32(d), [12H,CH(<u>Me</u>)$_2$]	102.9(A);99.0(B),80.6(C), 79.4(D),32.7(E),22.4(F),19.1(G).
$[Ru_2(\mu\text{-}Br)_3(\eta^6\text{-p-cymene})_2]PF_6$	5.64(AB), [8H,C_6H_4];2.84(se), [2H,C<u>H</u>(Me)$_2$];2.24(s), [6H,p-Me];1.30(d), [12H,CH(<u>Me</u>)$_2$].	103.9(A),99.1(B),80.2(C), 80.0(D),32.8(E),22.6(F),19.7(G).
$[Ru_2(\mu\text{-}I)_3(\eta^6\text{-p-cymene})_2]PF_6$	5.66(AB), [8H,C_6H_4];2.90(se), [2H,C<u>H</u>(Me)$_2$];2.34(s), [6H,p-Me];1.30(d), [12H,CH(<u>Me</u>)$_2$].	106.0(A),99.6(B),81.3(C), 80.5(D),33.2(E),22.9(F),20.7(G).
$[Os_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2]BF_4$	6.64(s).	73.8.
$[OsRu(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2]BF_4$ [c]	6.64(s), [6H,Os-C_6H_6];6.06(s), [6H,Ru-C_6H_6].	73.6 (Os-C_6H_6);82.2 (Ru-C_6H_6).
$[RuCl_2(\eta^6\text{-p-cymene})]_2$ [d]	5.45(AB), [8H,C_6H_4];2.93(se), [2H,C<u>H</u>(Me)$_2$];2.17(s), [6H,p-Me]; 1.29(d), [12H,CH(<u>Me</u>)$_2$].	100.8(A),96.5(B),81.1(C), 80.3(D),30.4(E),21.9(F), 18.7(G).

Table 2.4(cont).

Compound	^{1}H n.m.r.ᵃ	^{13}C n.m.r.ᵇ
$[RuBr_2(\eta^6\text{-p-cymene})]_2$[d]	5.43(AB),[8H,C_6H_4];2.95(se),[2H,C<u>H</u>(Me)$_2$];2.20(s),[6H,p-Me];1.26(d),[12H,CH(<u>Me</u>)$_2$].	102.0(A),96.7(B),81.2(C),81.1(D),30.7(E),22.2(F),19.2(G).
$[RuI_2(\eta^6\text{-p-cymene})]_2$[d]	5.48(AB),[8H,C_6H_4];3.01(se),[2H,C<u>H</u>(Me)$_2$];2.34(s),[6H,p-Me];1.24(d),[12H,CH(<u>Me</u>)$_2$].	104.2(A),97.4(B),82.4(C),81.9(D),31.3(E),22.6(F),20.1(G).

s = singlet, d = doublet, se = septet. [a]XL 100(FT) n.m.r. spectra; [b]HA 100 n.m.r. spectra, both a and b referenced to $SiMe_4$ (internal lock); [c]n.m.r. parameters of these compounds obtained from spectra of mixtures (see section 2.5); [d]spectra recorded in $CDCl_3$ at 298K. The mesitylene and p-cymene ring carbons labelled as in the table are assigned as follows.



Chapter 3

Syntheses and Reactions of Some Triple Hydroxo and Alkoxo Bridged η^6-Arene Complexes of Ruthenium(II)

3.1 Introduction

Maitlis and Kang[46] have shown that the triple hydroxo-bridged cation $\left[Rh_2(\mu\text{-}OH)_3(\eta^5\text{-}C_5Me_5)_2\right]^+$ (8b) can be isolated either as the chloride or tetraphenylborate salts, from the reaction of $\left[RhCl_2(\eta^5\text{-}C_5Me_5)\right]_2$ with aqueous NaOH. Donald Robertson[113] extended this reaction to the isoelectronic compounds $\left[MX_2(\eta^6\text{-arene})\right]_2$ (M = Ru, X = Cl^-, Br^-; arene = C_6H_6; X = Cl^-, arene = 1,3,5-$C_6H_3Me_3$; M = Os, X = Cl^-, arene = C_6H_6) and claimed to have isolated the complexes $\left[M_2(\mu\text{-}OH)_3(\eta^6\text{-arene})_2\right]Y$ (Y = Cl^-, Br^-, BPh_4^-).

These complexes were found to be stable towards bridge cleavage, in marked contrast to the analogous halo bridged compounds which react with Lewis bases L to give $\left[RuX(\eta^6\text{-arene})L_2\right]^+$ and $RuX_2(\eta^6\text{-arene})L$ (L = tertiary phosphine, pyridine, Et_2S etc.) (see Chapter 2). However, when the hydroxo benzene complex was refluxed in methanol or ethanol, the corresponding triple alkoxo bridged compounds were formed. With other alcohols such as n-butanol or isopropanol, facile decomposition occurred and no ruthenium complexes could be isolated. The alkoxo complexes are thought to form via the protonation of the hydroxide bridged complex by the weak acid ROH to give monomeric aquo species which then react with OR^- to give alkoxo species, and these combine to give the triple alkoxo bridged cation via a similar mechanism to that proposed for the formation of the triple halide bridged complexes (see Fig. 2.1. p.45).

The triple hydroxo bridged complex $\left[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}C_6H_6)_2\right]BPh_4$ was also prepared by the reaction of $\left[RuCl_2(\eta^6\text{-}C_6H_6)\right]_2$ with excess Na_2CO_3 in water.[113]

When a 1:1 molar ratio of Na_2CO_3 and an excess of Na_2SO_4 was used however, the novel tetrameric complex $\left[RuOH(\eta^6\text{-}C_6H_6)\right]_4\left[SO_4\right]_2 \cdot 12H_2O$ (63) was isolated. The formulation of this compound was confirmed by X-ray crystallography,[113,121] and it was shown to have a cubane structure with ruthenium and hydroxo entities arranged at alternate vertices.(see section 2.4. p.51).

Attempts to synthesise other cations of type $\left[Ru_2X_3(\eta^6\text{-arene})_2\right]^+$ ($X = OH^-$, OR^-) and $\left[Ru(OH)(\eta^6\text{-arene})\right]_4^{4+}$ have now been made, and these attempts are described in this chapter.

3.2 Reinvestigation of the initial product from the reaction of $\left[RuCl_2(\eta^6\text{-}C_6H_6)\right]_2$ with excess of aqueous NaOH or Na_2CO_3.

The initial product from the reaction of $\left[RuCl_2(\eta^6\text{-}C_6H_6)\right]_2$ with excess of NaOH or Na_2CO_3 in water followed by addition of $NaBPh_4$ shows two ν(OH) vibrations at 3615 cm^{-1} and 3520 cm^{-1} with a shoulder at 3530 cm^{-1} in its mull ir. spectrum. On recrystallisation from acetone, only one ν(OH) stretch at 3530 cm^{-1} was observed. The ^1H n.m.r. spectrum (in d^6-Me_2CO or d^3-$MeNO_2$) of the initial product shows a major resonance at δ = 5.33 ppm. and another weak one at 5.56 ppm. attributable to η^6-C_6H_6 ligands. The resonance at 5.56 ppm. grows in intensity when the solution is aged and a precipitate forms in the tube. This precipitation occurs much more rapidly in d^6-Me_2CO than in d^3-$MeNO_2$. The precipitate was shown to be a deuterated complex by ir. spectroscopy which showed bands at about 2600 cm^{-1} attributable to ν(OD) vibrations. The compound recrystallised from acetone shows a single η^6-C_6H_6 resonance at δ = 5.56 ppm. when reexamined in d^3-$MeNO_2$.

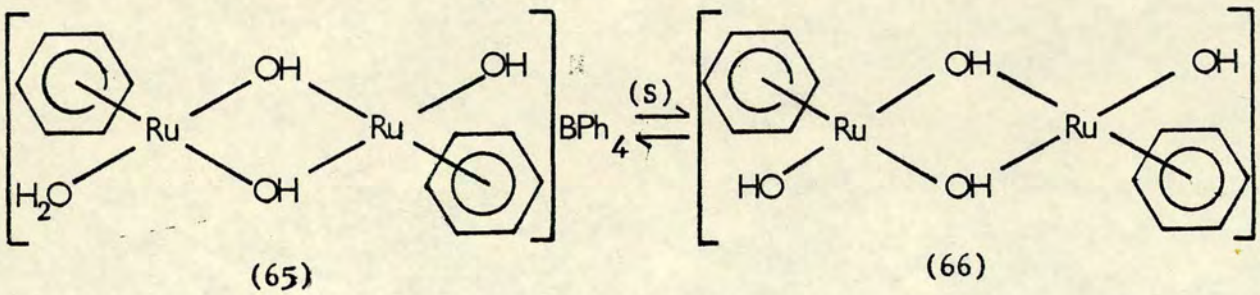
The ^1H n.m.r. spectrum of the initial product was originally interpreted[113] as being due to a mixture of the cations $\left[Ru_2(\mu\text{-}OD)_3\right.$-

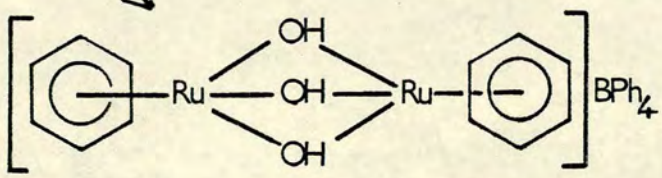
$(\eta^6\text{-}C_6H_6)_2]^+$ (δ = 5.33 ppm.) and $[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}C_6H_6)_2]^+$ (δ = 5.56 ppm.), but since the deuterated complexes are precipitated from solution and the initial major resonance is at 5.33 ppm., this explanation seems unlikely. Furthermore, a change of ca. 0.20 ppm. in the chemical shift of the benzene ring resonance simply by changing OH^- for OD^- groups is, on reflection, also improbable. The appearance of two ν(OH) vibrations was originally ascribed[113] to some distortion of the solid state structure, away from the idealised D_{3h} configuration, which should show only one ν(OH) vibration. A better interpretation of the ir. and ^1H n.m.r. spectra is that the initial product is mainly the double hydroxo bridged cation (65) which would give two ν(OH) vibrations in its ir. spectrum. However, in solution, this complex would be expected to give two closely separated $\eta^6\text{-}C_6H_6$ resonances, but even at very high resolution this was not observed. This could be explained by invoking a fast intra-molecular rearrangement process involving terminal and bridging hydroxo groups at ambient temperature. Unfortunately, since the rearrangement to the triple bridged cation is so rapid in $d^6\text{-}Me_2CO$, such that at low temperature (-90°C) the ^1H n.m.r. spectrum shows only this complex, any splitting of the resonance at δ = 5.33 ppm. due to the "freezing out" of the postulated hydroxo exchange process could not be observed. Another problem is that the chemical shift difference of ca 0.20 ppm. between this proposed cation (65) (5.33 ppm.) and the genuine triple bridged cation (67) (5.56 ppm.) is surprising since they are not very dissimilar. Therefore, a better explanation for both the inability to observe two benzene resonances and this large separation in chemical shift might be that , in solution, complex (65) is readily deprotonated to give the compound (66) and $HBPh_4$ (see Fig. 3.1). The chemical shift

difference between (66) and (67) is now appropriate for that between a neutral complex and a cationic one (cf. that between $\left[Ru_2(\mu\text{-}X)_3(\eta^6\text{-p-cymene})_2\right]PF_6$ and $\left[RuX_2(\eta^6\text{-p-cymene})\right]_2$ of ca. 0.20 ppm. ($X = Cl^-$, Br^-, I^-)).(see Chapter 2. Table 2.4). Furthermore, the benzene resonances would be expected to be magnetically equivalent in compound (66).and, as shown in Table 3.1, a mixture of (66) and $HBPh_4$ would behave as a 1:1 electrolyte in CH_3NO_2.

Fig. 3.1.

Postulated rearrangement processes for $\left[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}C_6H_6)_2\right]BPh_4$.





(67)

Finally, the product from reaction of $\left[OsCl_2(\eta\text{-}C_6H_6)\right]_2$ with excess of NaOH or Na_2CO_3[113] exhibited similar behaviour. The initial product showed two ν(OH) vibrations at 3580 cm^{-1} and 3530 cm^{-1} and a major resonance at δ = 5.93 ppm. and a smaller one at 6.13 ppm. in the ^1H n.m.r. spectrum in d^6-Me_2CO and at 5.97 ppm. and 6.08 ppm. in d^3-$MeNO_2$.

3.3 Reactions of $[RuCl_2(\eta^6\text{-arene})]_2$ with aqueous NaOH or Na_2CO_3 (arene = 1,3,5-$C_6H_3Me_3$, p-$MeC_6H_4CH(Me)_2$, C_6H_5OMe).

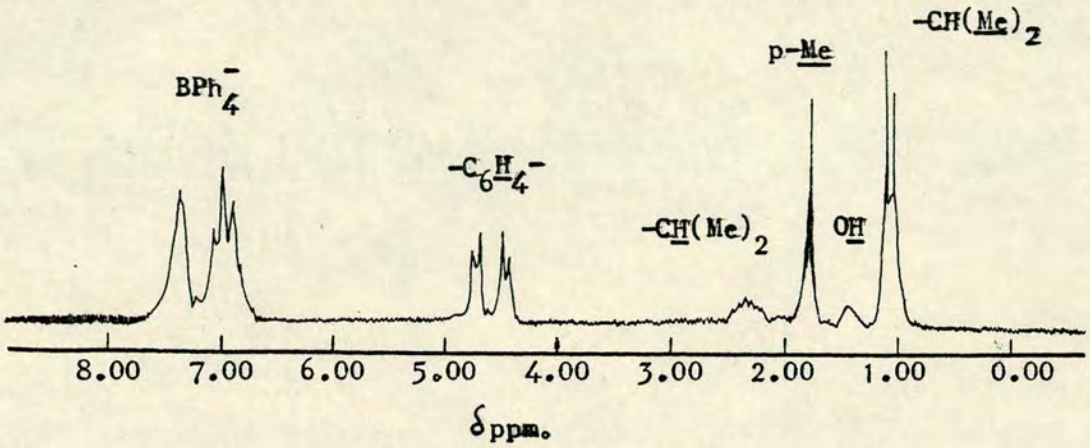
Unlike the reactions of the unsubstituted arene compounds $[MCl_2(\eta^6\text{-}C_6H_6)]_2$ (M = Os, Ru) with an excess of aqueous NaOH or Na_2CO_3 which gave initial products showing two ν(OH) vibrations, Donald Robertson[113] showed that the mesitylene compound reacted under the same conditions to give a product showing only one ν(OH) vibration in its ir. spectrum and one set of resonances in its ^{1}H n.m.r. spectrum, attributable to the protons of the η^6-$C_6H_3Me_3$ ligands. The compound isolated was shown to be the genuine triple bridged complex $[Ru_2(\mu\text{-OH})_3(\eta^6\text{-}C_6H_3Me_3)_2]Y$ (Y = Cl^-, BPh_4^-), and there was no evidence for formation of any double bridged complexes analogous to (65) and (66). Unequivocal proof of this formulation has now been obtained by X-ray crystallography[125] when Y = Cl^-. It was also found that although a tetramer $[RuOH(\eta^6\text{-}C_6H_6)]_4[SO_4]_2\cdot 12H_2O$ (63) was formed when $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ and Na_2CO_3 were reacted in 1:2 molar ratio in the presence of excess of Na_2SO_4, no such complex was formed when the analogous mesitylene compound was used. In an attempt to clarify the factors which determine the products from these reactions, the compounds $[RuCl_2(\eta^6\text{-arene})]_2$ (arene = p-$MeC_6H_4CH(Me)_2$, C_6H_5OMe) were reacted similarly.

The reaction of $[RuCl_2(\eta^6\text{-p-cymene})]_2$ with an excess of NaOH or Na_2CO_3 in water gave a complex showing one ν(OH) vibration at 3550 cm^{-1} in its ir. spectrum. The ^{1}H n.m.r. spectrum consisted of BPh_4^- multiplets, an AB quartet at δ = 4.76 ppm., a septet at 2.49 ppm., a singlet at 1.90 ppm., a broad singlet at 1.65 ppm. and a doublet at 1.18 ppm. (see Fig. 3.2). Integration showed the ratio of these resonances to be 20:8:2:6:3:12 respectively, indicating that the compound is $[Ru_2(\mu\text{-OH})_3(\eta^6\text{-p-cymene})_2]BPh_4$

(see Table 3.3 for assigning of resonances).

Fig. 3.2.

^{1}H n.m.r. spectrum at 298K of $\left[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}p\text{-}cymene)_2\right]BPh_4$ in $CDCl_3$.



Analysis (C,H) fits well for this formulation (see experimental section 3.6, Table 3.2), and further support for this comes from conductivity measurements. In nitromethane, a molar conductivity Λ_m = 70 ohm^{-1} cm^2 mol^{-1}, for a 10^{-3} mol dm^{-3} solution is obtained and a plot of $\Lambda_o - \Lambda_e$ vs $C_e^{\frac{1}{2}}$ gives a straight line of slope 100 which is consistent with the presence of a 1:1 electrolyte (see Table 3.1. for values found for other electrolytes).

The reaction of the dimer $\left[RuCl_2(\eta^6\text{-}C_6H_5OMe)\right]_2$ with excess of aqueous NaOH or Na_2CO_3 gave a product which showed two ν(OH) vibrations at 3560 cm^{-1} and 3500 cm^{-1} in its ir. spectrum. Unfortunately, the ^{1}H n.m.r. spectrum in d^6-Me_2CO was very complex and could not be satisfactorily interpreted as due to either $\left[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}C_6H_5OMe)_2\right]$-$BPh_4$ and/or "$\left[Ru_2(\mu\text{-}OH)_2(OH)(H_2O)(\eta^6\text{-}C_6H_5OMe)_2\right]BPh_4$". Furthermore, the reaction with NaOH is accompanied by extensive decomposition, which is probably due to the formation of unstable η^5-cyclohexadienyl intermediates by nucleophilic addition of OH^- to the anisole ring.

Table 3.1.

Conductivity data for various electrolytes in nitromethane.

Compound	Λ_m ($ohm^{-1}cm^2mol^{-1}$)	slope	ion type	Ref.
$[Ru_2(\mu\text{-}Cl)_3(PEt_2Ph)_6]Cl$	85.5	151	1:1	120
$Na[BPh_4]$	100	216	1:1	120
$[Pd_2(PPh_2)_2(Ph_2PC_2H_4PPh_2)_2][ClO_4]_2$	192	560	2:1	126
$[Ni(O\text{-}Phen)_3]Cl_2$	118	420	2:1	126
$[Co(bipy)_3][ClO_4]_3$	144	1020	3:1	126
$[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2]PF_6$	82	207	1:1	113
$[Ru_2(\mu\text{-}Cl)_3(PMe_2Ph)_6]PF_6$	75	190	1:1	113
$[Ru_2(\mu\text{-}OMe)_3(\eta^6\text{-}C_6H_3Me_3)_2]BPh_4$	55.4	176	1:1	(This work)
$[Ru_2(\mu\text{-}OH)_2(OH)(H_2O)(\eta^6\text{-}C_6H_6)_2]BPh_4$	61	214	1:1	113
$[Ru_2(OMe)_3(\eta^6\text{-}C_6H_6)_2]PF_6$	68	245	1:1	113

Although these results are not fully comprehensive, in that reactions of other substituted arene complexes with OH^- and CO_3^{2-} ions need to be investigated, it seems that the greater the degree of substitution of the arene ring, the greater the tendency to form the triple hydroxo bridged complex since no evidence for the formation of double hydroxo bridged intermediates analogous to (65) has been found for arene = p-cymene or mesitylene.

Finally, all attempts to synthesise tetramers analogous to (63) (see Chapter 2. p.51) from the complexes $[RuCl_2(\eta^6\text{-arene})]_2$ (arene = C_6H_5OMe, $1,3,5\text{-}C_6H_3Me_3$, $p\text{-}MeC_6H_4CH(Me)_2$) and stoichiometric amounts of Na_2CO_3 were unsuccessful, only binuclear complexes being obtained. The most likely explanation for this is the presence of steric constraints arising from substituents on the arene ring which inhibit the formation of the tetramers, and since the rings are much further apart

in the triple hydroxo bridged complexes, these compounds are preferentially formed.

3.4 The syntheses and characterisation of some alkoxo bridged complexes of ruthenium.

Donald Robertson has shown that the triple alkoxo bridged complexes $\left[Ru_2(\mu\text{-}OR)_3(\eta^6\text{-}C_6H_6)_2\right]BPh_4$ (R = Me, Et) were produced in good yields by two separate routes.[113] These were by reaction of the dimer $\left[RuCl_2(\eta^6\text{-}C_6H_6)\right]_2$ with freshly prepared NaOR in ROH followed by addition of excess of $NaBPh_4$ or by refluxing the triple hydroxo bridged complex $\left[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}C_6H_6)_2\right]BPh_4$ in the appropriate alcohol. When long chain alcohols such as n-butanol or isopropanol were used, extensive decomposition occurred and no ruthenium complexes could be isolated from the reaction mixture. This decomposition was thought to proceed via ruthenium hydride formation generated by β-elimination from intermediate alkoxo species. Evidence for hydride formation comes from a very recent report[48] on the isolation of the complexes $\left[Ru_2(\mu\text{-}H)_2(\mu\text{-}X)(\eta^6\text{-arene})_2\right]PF_6$ (10) ($X = Cl^-$, arene = C_6Me_6, 1,3,5-$C_6H_3Me_3$; $X = H^-$, arene = 1,3,5-$C_6H_3Me_3$) (see section 1.4. p.15) obtained by reaction of $\left[RuCl_2(\eta^6\text{-arene})\right]_2$ with aqueous solutions containing isopropoxide ions.

Similar hydride complexes are probably formed for the benzene compounds with longer chain alkoxides, but due to the comparative weakness* of the ruthenium benzene bonds, loss of benzene also occurs

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*The strength of the metal to arene bond has been shown to increase with the number of methyl substituents on the ring, by means of mass spectral studies[127] on $Cr(\eta^6\text{-arene})_2$ and by microcalorimetric[128] measurements on $Cr(\eta^6\text{-arene})(CO)_3$ complexes.

and these compounds could not be isolated. However, since both the triple bridged methoxo and ethoxo complexes have been synthesised from the benzene compound, attempts were made to see if analogous mesitylene and p-cymene complexes could be synthesised by similar routes.

The reaction of $\left[RuCl_2(\eta^6\text{-}C_6H_3Me_3)\right]_2$ with freshly prepared NaOMe in methanol, gives, after addition of excess $NaBPh_4$, a yellow microcrystalline solid (see experimental section 3.7). The ^1H n.m.r. spectrum (see Table 3.3) of this solid in d^6-acetone indicates that it is the triple methoxo bridged complex $\left[Ru_2(\mu\text{-}OMe)_3(\eta^6\text{-}C_6H_3Me_3)_2\right]BPh_4$. The integration of the ^1H n.m.r. spectrum showing the ratio of BPh_4^- : $C_6H_3Me_3$: OMe^- of 1:2:3 and the analysis (C,H) fits well for this formulation (see Tables 3.2 and 3.3) and further support comes from conductivity measurements. In nitromethane, a molar conductivity, $\Lambda_m = 55.4$ ohm^{-1}cm^{2}mol^{-1}, for a 10^{-3} mol dm^{-3} solution is obtained and a plot of $\Lambda_o - \Lambda_e$ vs $C_e^{\frac{1}{2}}$ gives a straight line of slope 176 which is consistent with a 1:1 electrolyte (see Table 3.1 p.90). However, when this reaction was carried out in the same volume of solvent but using twice as much starting material, the product shows four $\eta^6\text{-}C_6H_3Me_3$ resonances in the ^1H n.m.r. spectrum, one of which corresponds to the triple methoxy bridged complex. The other resonances must presumably arise from complex cations since the products are trapped out with $NaBPh_4$ and they are probably methoxo containing intermediates, such as $\left[RuOMe(MeOH)_2(\eta^6\text{-}C_6H_3Me_3)\right]^+$, $\left[Ru_2(\mu\text{-}OMe)_2(OMe)(MeOH)(\eta^6\text{-}C_6H_3Me_3)\right]^+$ etc.. No attempts however, were made to separate and study these species in more detail.

A similar reaction with NaOEt in ethanol produces extensive decomposition together with a small amount of yellow solid on addition of excess $NaBPh_4$. Although elemental analysis for this solid fits quite well for $\left[Ru_2(\mu\text{-}OEt)_3(\eta^6\text{-}C_6H_3Me_3)_2\right]BPh_4$ (see experimental

section 3.6, Table 3.2) and conductivity measurements indicate the presence of a 1:1 electrolyte, (Λ_m = 49 $ohm^{-1}cm^2mol^{-1}$ for a 10^{-3} mol dm^{-3} solution in nitromethane), the ^1H n.m.r. spectrum in d^6-Me_2CO shows the solid to be a mixture of two components. Thus, two co-ordinated mesitylene resonances at δ =5.10 ppm.and 5.00 ppm.are observed in the intensity ratio 3:1 as well as co-ordinated OEt^- groups which give a quartet pattern at δ = 4.58 ppm.. A similar material is produced when $\left[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}C_6H_3Me_3)_2\right]BPh_4$ is refluxed in ethanol although the ratio of the two resonances at 5.10 and 5.00 ppm. due to co-ordinated mesitylene moeities is now 6:1 respectively. If it is assumed that the major resonance in each case is due to the triple ethoxo bridged complex, then the other presumably arises from some cationic complex which is also a 1:1 electrolyte. This product cannot be fully characterised from the ^1H n.m.r. spectrum since the intensity of any associated ethoxo groups are either very weak or they coincide with those due to the triple bridged complex. By analogy with the benzene hydroxo complexes (65),(66) and (67) (see section 3.2), a similar rearrangement process may be occurring. However, in this case the major species trapped out with $NaBPh_4$ appears to be the triple bridged complex. Alternatively, the smaller component might be a monomeric cation such as $\left[Ru(OEt)(EtOH)_2(\eta^6\text{-}C_6H_3Me_3)\right]^+$ trapped out by the bulky BPh_4^- anion. Again, no attempts have been made to separate these compounds on a preparative scale.

The reaction of $\left[RuCl_2(\eta^6\text{-p-cymene})\right]_2$ with an excess of NaOMe in methanol also gives a yellow solid on addition of $NaBPh_4$. Analysis (C, H) and conductivity measurements (see experimental section Table 3.2) again suggest that this complex is $\left[Ru_2(\mu\text{-}OMe)_3(\eta^6\text{-p-cymene})_2\right]BPh_4$. However, the ^1H n.m.r. spectrum in $CDCl_3$ shows this product to be a mixture of two components which contain co-ordinated OMe^- groups

in the intensity ratio 6:1 at δ = 4.17 ppm. and 4.06 ppm. respectively. A further weak resonance at δ = 3.38 ppm. could be due to terminal OMe^- groups. Thus, the two complexes are probably $\left[Ru_2(\mu\text{-}OMe)_3(\eta^6\text{-p-cymene})_2\right]BPh_4$ and $Ru_2(\mu\text{-}OMe)_2(OMe)_2(\eta^6\text{-p-cymene})_2$, the latter being formed by deprotonation in solution of $\left[Ru_2(\mu\text{-}OMe)_2(OMe)(MeOH)(\eta^6\text{-p-cymene})_2\right]BPh_4$ by a mechanism similar to that in shown Fig. 3.1.

The reactions of $\left[RuCl_2(\eta^6\text{-p-cymene})\right]_2$ with NaOEt/EtOH and $\left[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-p-cymene})_2\right]BPh_4$ with ethanol give similar mixtures of products (see experimental section 3.6 and Tables 3.2 and 3.3).

Since, when OEt^- ions or ethanol are used in these reactions, extensive decomposition occurs, there is the possibility that this is due to hydride formation via β elimination from unstable alkoxo intermediates. However, ir. and ^1H n.m.r. (low frequency) studies on the various products reveal no evidence for any direct Ru-H interactions in these reactions although it is highly likely that this is the explanation for the extensive decomposition observed.

In conclusion, it appears that product mixtures are often obtained in these reactions because the BPh_4^- anion is very indiscriminate in precipitating a range of cationic species from concentrated solutions.

This indiscriminate precipitation was also observed when $\left[RuCl_2(\eta^6\text{-}C_6H_6)\right]_2$ was shaken with $NaBPh_4$ in methanol, This gave a product which was originally formulated as $\left[Ru_2(\mu\text{-}Cl)_2(\mu\text{-}OMe)(\eta^6\text{-}C_6H_6)_2\right]BPh_4$.[113] However, the ^1H n.m.r. spectrum of this solid has now been recorded in $d^3\text{-}MeNO_2$ (where bridge cleavage is unlikely) and this clearly shows that three species are present with co-ordinated benzene resonances at δ = 5.91, 5.76 and 5.43 ppm. respectively. It is interesting to note that a similar reaction with NH_4PF_6 gave only $\left[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2\right]PF_6$ in high yield,[113] and therefore, use of PF_6^- or BF_4^- in future studies on $\left[RuCl_2(\eta^6\text{-arene})\right]_2/RO^-$ reactions

might be more successful in "trapping out" clean products. Working at lower concentrations might also help to avoid precipitation of some of the cationic monomeric intermediates.

3.5 Some preliminary studies on reactions of $[Ru_2(\mu\text{-}OR)_3(\eta^6\text{-arene})_2]BPh_4$ (R = H, Me; arene = C_6H_6, 1,3,5-$C_6H_3Me_3$) and $[Ru(\eta^6\text{-}C_6H_6)(solv)_3]^{2+}$ (solv = MeOH, Me_2CO, MeCN).

The original aim of this work was to synthesise complexes which contained a stable $-Ru(\mu\text{-}X)_3Ru-$ unit such as $[Ru_2(\mu\text{-}X)_3(\eta^6\text{-}C_6H_6)_2]^+$ (X = halide, OH^-, OR^- (R = Me, Et), and then attempt to displace the benzene ring with various Lewis bases without cleavage of the bridges, thus producing a wide range of new cations of type $[Ru_2(\mu\text{-}X)_3L_6]^+$ (L = C_5H_5N, AsR_3, etc.). However, it was found that the complex $[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}C_6H_6)_2]PF_6$ (9a) reacted with Lewis bases under mild conditions to give the bridge cleaved products $RuCl_2(\eta^6\text{-}C_6H_6)L$ and $[RuCl(\eta^6\text{-}C_6H_6)L_2]PF_6$. Under reflux, the co-ordinated benzene group was displaced and with PMe_2Ph the complex $[Ru_2(\mu\text{-}X)_3(PMe_2Ph)_6]PF_6$ was in fact isolated. However, this is thought to form via $RuCl_2(PMe_2Ph)_4$, generated in situ by the displacement of benzene from the bridge cleaved products rather than direct displacement from the binuclear complex.[113] It was known that the hydroxy bridged complexes $[M_2(\mu\text{-}OH)_2L_4][BF_4]_2$ (M = Pt, L = PEt_3, PPh_3, C_5H_5N; M = Pd, L = PPh_3) were extremely stable towards bridge cleavage,[129] in contrast to their chloro-bridged analogues, and it was therefore hoped that the complex $[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}C_6H_6)_2]BPh_4$ would be stable towards bridge cleavage with Lewis bases, but that the co-ordinated benzene rings might be displaced. As expected, the hydroxo bridges were extremely stable, but unfortunately, the benzene ligands could not be displaced either.[113]

The hydroxo protons are not susceptible to attack by strong bases as was demonstrated by the reaction of $[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}C_6H_3Me_3)_2]-$

BPh_4 with 1,8-bis-(dimethylamino) naphthalene ("proton sponge") which gave the starting compound unchanged, even after refluxing in acetone for several hours. This lack of reactivity towards bases might be indicative of the presence of substantial inter- or intra-molecular hydrogen bonding interactions. If this is correct, then the analogous alkoxo bridged complexes $\left[Ru_2(\mu\text{-}OR)_3(\eta^6\text{-arene})_2\right]BPh_4$ (R = Me, Et; arene = C_6H_6, 1,3,5-$C_6H_3Me_3$) where such interactions are not possible would be expected to cleave readily. However, at this juncture due to lack of time, only preliminary reactions have been carried out on these alkoxo complexes and as yet , no conclusive evidence for bridge cleavage has been found. Thus, for example, although refluxing the complex $\left[Ru_2(\mu\text{-}OMe)_3(\eta^6\text{-}C_6H_3Me_3)_2\right]BPh_4$ with excess of PPh_3 in acetone gives no reaction, ^1H and $^{31}P\text{-}\{H\}$ n.m.r. spectroscopic studies suggest that $P(OMe)_3$ does react, under reflux conditions to give a mixture of as yet unidentified products. Much more work in this area is required before an explanation for the high stability of these hydroxo bridged complexes is found.

Earlier, Maitlis and co-workers have shown that the dications $\left[M(\eta^5\text{-}C_5Me_5)(Me_2CO)_3\right]^{2+}$ (M = Rh, Ir) were very useful intermediates for synthesising a range of new complexes. For example, reactions with Lewis bases[130] readily gave the complexes $\left[M(\eta^5\text{-}C_5Me_5)L_3\right]\left[PF_6\right]_2$ (M = Rh, Ir; L = $P(OMe)_3$, $P(OEt)_3$, PMe_2Ph, etc.) and with arenes,[59] the mixed sandwich complexes $\left[M(\eta^5\text{-}C_5Me_5)(\eta^6\text{-arene})\right]\left[PF_6\right]_2$ (M = Rh, arene = benzene, toluene, m-xylene, mesitylene, fluorene, indole; M = Ir, arene = toluene, m-xylene, naphthalene, phenanthrene, indene, indole, fluorene) were isolated and fully characterised.

These tris-solvent species were prepared <u>in situ</u> by the reaction of $\left[MCl_2(\eta^5\text{-}C_5Me_5)\right]_2$ with $AgPF_6$ and when co-ordinating solvents were used, the complexes $\left[M(\eta^5\text{-}C_5Me_5)L_3\right]\left[PF_6\right]_2$ (L = Me_2SO, MeCN,

C_5H_5N) could be isolated.[59] Thus, it was expected that the isoelectronic compound $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ would react similarly and therefore a number of preliminary reactions were examined. For example, treatment of $[RuCl_2(\eta^6\text{-}C_6H_6)]_2$ with $AgPF_6$ in MeCN led to isolation of $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3][PF_6]_2$ (see experimental section 3.6). This complex shows one ν(CN) vibration at 2290 cm^{-1} * as expected for a molecule of D_{3h} symmetry and its ^1H n.m.r. spectrum in MeCN shows resonances at δ = 6.20 ppm. and 3.10 ppm. in the ratio 2:3 due to co-ordinated benzene and MeCN respectively. The analogous complexes $[Ru(\eta^6\text{-arene})L_3][PF_6]_2$ (arene = 1,3,5-$C_6H_3Me_3$, C_6Me_6; L = Me_2SO, C_5H_5N, PhCN, $P(OMe)_3$) have recently been synthesised independently by a very similar route.[132]

The reactions of the complex $[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3][PF_6]_2$ with an excess of the tertiary phosphines $PMePh_2$ and PMe_2Ph were investigated but in each case, a mixture of products was generated. With PMe_2Ph elemental analysis, ^1H n.m.r. and $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopic studies indicate that the product is a mixture of the dications $[Ru(\eta^6\text{-}C_6H_6)(PMePh_2)_3]^{2+}$ and $[Ru(\eta^6\text{-}C_6H_6)(PMePh_2)_2MeCN]^{2+}$ in 63% and 37% yields respectively. Thus, in d^6-Me_2CO the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum shows a major resonance at δ = 9.8 ppm. and a smaller one at 17.7 ppm. as well as a septet at -144.8 ppm. due to PF_6^- ($^1J(PF)$ = 708Hz). The ^1H n.m.r. spectrum in d^6-Me_2CO shows two co-ordinated benzene resonances at δ = 6.66 ppm. and 6.42 ppm. respectively. Furthermore, a "pseudo triplet"**

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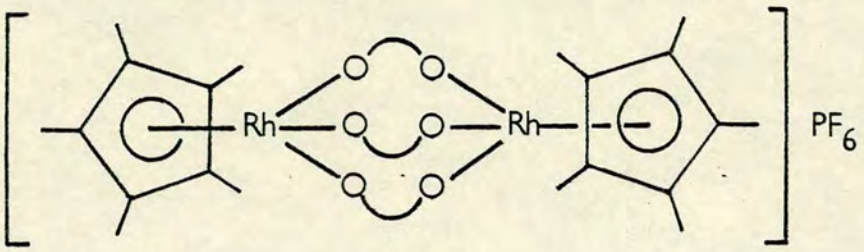
* Another band at 2320 cm^{-1} is attributed to the combination band of a symmetric CH_3 deformation and C-C stretching vibration (cf. $RuCl_2(CO)MeCN(C_8H_{12})$ which has two ir. vibrations at 2305 and 2340 cm^{-1} respectively.[131] ** A "pseudo-triplet" pattern consists of a sharp doublet with a broad hump situated between the doublet and signifies a relatively large J(PP) compared to the $|J(PH) + J(PH)'|$ value cf. $[Ru_2Cl_3(PMe_2Ph)_6]Cl$.[87b]

at δ = 2.34 ppm. decouples to a singlet on irradiation at a frequency corresponding to the ^{31}P resonance at 9.78 ppm. and thus, this can be attributed to the complex $\left[Ru(\eta^6\text{-}C_6H_6)(PMePh_2)_3\right]\left[PF_6\right]_2$ containing three facial $PMePh_2$ groups. The methyl phosphine and MeCN resonances due to the other complex are not observed probably because these are masked by strong residual acetone and water resonances respectively. A similar mixture of products is found when PMe_2Ph is used . The $^{31}P\text{-}\{^1H\}$n.m.r. spectrum, besides showing free phosphine and phosphine oxide signals, gives two resonances at δ = 9.4 and 4.9 ppm. The ^1H n.m.r. spectrum was not very informative due to the masking effects of the various impurities present. The reaction of $\left[Ru(\eta^6\text{-}C_6H_6)(solv)_3\right]^{2+}$ (solv = MeOH) with PMe_2Ph also gives a product showing a resonance at δ= 4.9 ppm in its $^{31}P\text{-}\{^1H\}$n.m.r. spectrum as does the reaction of $\left[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}C_6H_6)_2\right]BPh_4$ with excess of PMe_2Ph in the presence of HPF_6. Thus, this resonance is probably due to the $\left[Ru(\eta^6\text{-}C_6H_6)(PMe_2Ph)_3\right]^{2+}$ cation and the other at δ = 9.37 ppm. can be assigned to the dication $\left[Ru(\eta^6\text{-}C_6H_6)(PMe_2Ph)_2MeCN\right]^{2+}$, since elemental analysis of the mixture shows the presence of nitrogen. Stepwise displacement of MeCN by tertiary phosphines has been observed for the complexes $WCl(\eta^3\text{-allyl})\text{-}(CO)_2(MeCN)_2$ (33)[80](see section 1.6 p.27) and also $\left[Rh(\eta^5\text{-}C_5Me_5)\text{-}(MeCN)_3\right]\left[PF_6\right]_2$.[130]

The tris-acetone complexes $\left[M(\eta^5\text{-}C_5Me_5)(Me_2CO)_3\right]\left[PF_6\right]_2$ (M = Rh, Ir) have been shown by Maitlis et al[59] to undergo a series of rearrangements in solution including partial hydrolysis of PF_6^- to generate the novel cation $\left[Rh_2(\mu\text{-}F_2PO_2)_3(\eta^5\text{-}C_5Me_5)_2\right]PF_6$. (68)



(68)

Very recently, similar complexes[132] have been isolated from $\left[Ru(\eta^6\text{-arene})(Me_2CO)_3\right]\left[PF_6\right]_2$ (arene = 1,3,5-$C_6H_3Me_3$, C_6Me_6). However, no benzene analogue has been reported and our earlier attempts to generate this led only to extensive decomposition which can be attributed to the relative strengths of the arene-ruthenium bonds (see footnote section 3.5 p.91).

Finally, the reaction of $\left[Ru(\eta^6\text{-}C_6H_6)(solv)\right]^{2+}$ (solv = MeOH) with hexamethylbenzene was carried out but no bis-arene complex could be isolated. However, the tris-acetone, solvate complexes $\left[Ru(\eta^6\text{-arene})(Me_2CO)_3\right]^{2+}$ have very recently been shown to react with other arenes[133] in the presence of acids such as HBF_4, HPF_6 or CF_3CO_2H to give the bis-arene complexes $\left[Ru(\eta^6\text{-arene})(\eta^6\text{-arene}')\right]\left[PF_6\right]_2$ in good yields (arene = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6; arene′ = C_6H_6, 1,3,5-$C_6H_3Me_3$, C_6Me_6, $C_{10}H_8$, $C_{14}H_{10}$, $C_6H_5C_6H_5$, C_6H_5OMe, C_6H_5Cl, $C_6H_5NMe_2$, C_6H_5OH, C_6H_5O, C_6H_5OMe, $C_6H_5CO_2Me$, $C_6H_5CO_2H$, $C_6H_5CF_3$). Although the presence of acid was not essential for many of these preparations, its presence greatly reduced the reaction time and increased the yields considerably, probably by helping to remove the co-ordinated acetone groups and minimise any possible side reactions.

In conclusion, these studies have helped to show that like the isoelectronic $\left[M(\eta^5\text{-}C_5Me_5)(solv)_3\right]^{2+}$ dications, the $\left[Ru(\eta^6\text{-arene})(solv)_3\right]^{2+}$ dications are very useful precursors for carrying out a wide range of

reactions. However, it must be admitted that recent independent studies by Bennett and co-workers[132,133] have been much more successful, largely because they worked with substituted arenes such as 1,3,5-$C_6Me_3H_3$ and C_6Me_6 which yielded much more stable products.

Nevertheless, the observation that the reaction of $\left[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}C_6H_6)_2\right]BPh_4$ with PMe_2Ph in the presence of HPF_6 gives $\left[Ru(\eta^6\text{-}C_6H_6)(PMe_2Ph)_3\right]^{2+}$ strongly indicates that an even better route to the bis-arene complexes for examplewould be to react the arene with the triple hydroxo bridged complexes in the presence of acid. If successful, this would avoid the use of the expensive compounds $AgPF_6$ and $AgBF_4$.

3.6 Experimental

Experimental details were as for those described in section 2.7 Chapter 2.

Chemicals.

As for section 2.7 plus,sodium sulphate and sodium carbonate (Evans Medical Ltd.); sodium hydroxide and triphenylphosphine (B.D.H.); silver nitrate (Johnson-Matthey); hexamethylbenzene (Koch-Light Ltd); sodium metal and acetonitrile (Fisons); "proton sponge" (Aldrich chemicals); dimethylphenylphosphine, methyldiphenylphosphine and trimethylphosphite (Maybridge Chemicals).

Starting Materials.

Prepared as described in section 2.7. The compounds $\left[Ru_2(\mu\text{-}OH)_2(OH)(H_2O)(\eta^6\text{-}C_6H_6)_2\right]BPh_4$, $\left[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}C_6H_6)_2\right]BPh_4$. acetone and $\left[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}C_6H_3Me_3)_2\right]BPh_4$ were synthesised as described elsewhere. (ref. 113).

Tri-μ-hydroxobis (η^6-p-cymene)ruthenium(II)tetraphenylborate.

Method A. The compound $\left[RuCl_2(\eta^6\text{-p-cymene})\right]_2$ (0.25g, 0.40 mmol) was dissolved in water (10 cm^3) and NaOH (2 pellets) was added. The

solution was stirred and gently warmed for two hours. It was then filtered and excess $NaBPh_4$ in water (5 cm^3) was added to give a gummy precipitate. Vigorous stirring for several hours gave a yellow, powdery precipitate. This was filtered off and washed with water and light petroleum (bp. 60-80°C); ν(OH)=3550 cm^{-1} (mull). Yield 32%.

Method B. The reaction was carried out as for method A, but an excess of Na_2CO_3 instead of NaOH was used. Yield 75%.

A similar reaction of the dimer $\left[RuCl_2(\eta^6\text{-}C_6H_5OMe)\right]_2$ with Na_2CO_3 gave, on addition of $NaBPh_4$, a colloidal precipitate which could be collected by centrifuging (see text section 3.3 p. for further discussion).

Tri-μ-methoxobis(η^6-mesitylene)ruthenium(II)tetraphenylborate.

The compound $\left[RuCl_2(\eta^6\text{-}C_6H_3Me_3)\right]_2$ (0.12g, 0.20 mmol) was stirred in freshly prepared NaOMe (Na metal (0.10g) in methanol (10 cm^3)) to give an orange solution. This was filtered and an excess of $NaBPh_4$ in methanol (5 cm^3) was added to give a copious yellow precipitate which was filtered and washed with methanol and diethylether. Yield 65% m.p. 203-205°C.

The following complexes were obtained as mixtures consisting mainly of the triple bridged complex plus another complex which is thought to be a double alkoxo bridged species (see section 3.4 for further discussion).

Tri-μ-methoxobis(η^6-p-cymene)ruthenium(II)tetraphenylborate.

Method A. The compound $\left[RuCl_2(\eta^6\text{-p-cymene})\right]_2$ (0.25g, 0.40 mmol) was dissolved in freshly prepared NaOMe (Na metal 0.2g. in methanol (20 cm^3)) to give a yellow solution. This was stirred vigorously for two hours, the solution filtered and an excess of $NaBPh_4$ in methanol (5 cm^3) was added. A yellow precipitate formed and this was filtered off and washed with methanol and diethylether. Yield 82%; m.p.156-158 C.

Method B. The complex $\left[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}p\text{-}cymene)_2\right]BPh_4$ (0.17g, 0.20 mmol) was refluxed in methanol (10 cm^3) for four hours. The solution was cooled and the yellow precipitate which had formed was filtered off and washed as in method A. Yield 78% (^1H n.m.r. spectra indicate that both methods give identical samples (see text section 3.4).

Tri-μ-ethoxobis(η^6-mesitylene)ruthenium(II)tetraphenylborate.

The complex $\left[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}C_6H_3Me_3)_2\right]BPh_4$ (0.16g, 0.20 mmol) was refluxed in ethanol (10 cm^3) for two hours. The solution was cooled and the yellow precipitate filtered off and washed with ethanol and diethylether.

The reactions of $\left[RuCl_2(\eta^6\text{-arene})\right]_2$ (arene = 1,3,5-$C_6H_3Me_3$, p-$MeC_6H_4CH(Me)_2$)with NaOEt/EtOH gave extensive decomposition and complex mixtures of products (see section 3.5 for discussion), as did the reaction of $\left[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}p\text{-}cymene)_2\right]BPh_4$ with ethanol.

(η^6-benzene)tris(acetonitrile)ruthenium(II)hexafluorophosphate.

The compound $\left[RuCl_2(\eta^6\text{-}C_6H_6)\right]_2$ (0.20g, 0.40 mmol) was stirred with $AgPF_6$ (0.40g; 1.60 mmol) in MeCN (10 cm^3) to give a yellow solution and a precipitate of AgCl which was removed by filtration through celite. The solvent was then removed under vacuo and the yellow powdery residue was washed with diethyl ether and dried in vacuo. Yield 67% m.p. 173°C (decomp.), ν(CN) = 2290 cm^{-1} additional band at 2320 cm^{-1} attributed to combination band of symmetric CH_3 deformation and C-C stretching vibration.

Analysis. Found; C,24.3%, H,2.3%, N,6.9%. Expected for $\left[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3\right]\left[PF_6\right]_2$, C,24.3%, H,2.6%, N,7.1%.

(η^6-Benzene)tris(methyldiphenylphosphine)ruthenium(II)hexafluorophosphate (A) and (η^6-benzene)bis(methyldiphenylphosphine)(acetonitrile)ruthenium(II) hexafluorophosphate(B).

The compound $\left[Ru(\eta^6\text{-}C_6H_6)(MeCN)_3\right]\left[PF_6\right]_2$ (0.15g, 0.25 mmol)

was refluxed in ethanol (20 cm^3) with $PMePh_2$ (0.3 cm^3, 2.0 mmol) for one hour. The solution was cooled and concentrated to give a yellow precipitate. This was filtered off and washed with diethyl ether. Analysis for a 67% to 37% mixture of A and B. Found C,48.0%, H,4.0%, N,0.40%, Expected C,48.2%, H,4.1%, N,0.40%.

Table 3.2.

Analytical and conductivity data for some hydroxo and alkoxo bridged complexes.

Compound	Found(%) C	Found(%) H	Calculated(%) C	Calculated(%) H	Λ_m ($ohm^{-1} cm^2 mol^{-1}$)[c]	Reference
$[Ru_2(\mu\text{-}OH)_2(OH)(H_2O)(\eta^6\text{-}C_6H_6)_2]BPh_4$[a]	56.5	4.9	57.9	5.0	61	113
$[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}C_6H_6)_2]BPh_4$.acetone	59.7	5.2	59.5	5.2	55	This work
$[Ru_2(\mu\text{-}OMe)_3(\eta^6\text{-}C_6H_3Me_3)_2]BPh_4$	63.3	6.2	63.2	6.3	50	" " " "
$[Ru_2(\mu\text{-}OEt)_3(\eta^6\text{-}C_6H_3Me_3)_2]BPh_4$[b]	63.4	6.5	63.8	6.7	49	" " " "
$[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}p\text{-cymene})_2]BPh_4$	63.1	6.3	62.9	6.1	70	" " " "
$[Ru_2(\mu\text{-}OMe)_3(\eta^6\text{-}p\text{-cymene})_2]BPh_4$[b]	63.7	6.4	63.9	6.5	49	" " " "
$[Os_2(\mu\text{-}OH)_2(OH)(H_2O)(\eta^6\text{-}C_6H_6)_2]BPh_4$[a]	45.4	3.7	46.7	4.0	83	113

a - Believed to be $[M_2(\mu\text{-}OH)_2(OH)_2(\eta^6\text{-}C_6H_6)_2][H.BPh_4]$ (M = Ru,Os) in solution (see sec. 3.2).

b - Thought to be mixture of $[Ru_2(\mu\text{-}OR)_3(\eta^6\text{-arene})_2]BPh_4$ and $[Ru_2(\mu\text{-}OR)_2(OR)_2(\eta^6\text{-arene})_2][HBPh_4]$ in solution.

c - 10^{-3} mol dm^{-3} solutions in nitromethane.

Table 3.3.

^{1}H and $^{13}C-\{^{1}H\}$ n.m.r. data for some hydroxo and alkoxo bridged complexes at 298K.

δ ppm

Compound	^{1}H n.m.r.	$^{13}C-\{^{1}H\}$ n.m.r.
$[Ru_2(\mu\text{-}OH)_2(OH)_2(\eta^6\text{-}C_6H_6)_2][HBPh_4]$ [ab]	5.33(s)[c]	77.8
$[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-}C_6H_6)_2]BPh_4$.acetone [a]	5.56(s),[c] [12H,C_6H_6]; 7.73(m) and 7.28(m), [20H,BPh_4].	79.4
$[Ru_2(\mu\text{-}OMe)_3(\eta^6\text{-}C_6H_3Me_3)_2]BPh_4$ [d]	5.08(s), [6H,C_6H_3]; 4.36(s), [9H,OMe]; 2.16(s), 18H,Me .7.72(m) and 7.27(m), [20H,BPh_4].	91.4(A);77.7(B);67.2(C); 17.4(D).
$[Ru_2(\mu\text{-}OEt)_3(\eta^6\text{-}C_6H_3Me_3)_2]BPh_4$ [bd]	5.10(s), [6H,C_6H_3]; 4.58(qu), [6H,$OC\underline{H}_2Me$]; 2.18(s), [18H,Me]; 1.40(t), [9H,$OCH_2\underline{Me}$].	
$[Ru_2(\mu\text{-}OH)_3(\eta^6\text{-p-cymene})_2]BPh_4$ [e]	4.76(AB), [8H,C_6H_4]; 2.49(se), [2H,$C\underline{H}(Me)_2$]; 1.90(s), [6H,p-Me]; 1.65(s), [3H,OH]; 1.18(d), [12H,$CH(\underline{Me})_2$]; 7.60(m) and 7.20(m), [20H,BPh_4].	96.4(A);93.0(B);77.4(C); 74.8(D);31.1(E);22.4(F); 17.9(G).
$[Ru_2(\mu\text{-}OMe)_3(\eta^6\text{-p-cymene})_2]BPh_4$ [be]	4.70(AB), [8H,C_6H_4]; 4.18(s), [9H,OMe]; 2.53(se), [2H,$C\underline{H}(Me)_2$]; 1.92(s), [6H,p-Me]; 1.18(d), [12H,$CH(\underline{Me})_2$].	96.4(A);91.4(B);76.9(C); 75.9(D);67.2(OMe);31.2(E); 22.3(F);18.1(G).

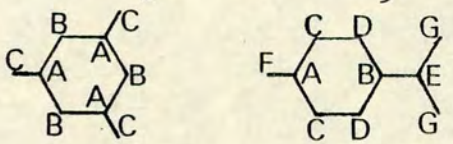
Table 3.3 cont.

Compound	^{1}H n.m.r.	^{13}C-{^{1}H}n.m.r.
$[Ru_2(\mu\text{-OEt})_3(\eta^6\text{-p-cymene})_2]BPh_4$ [be]	4.46(AB), [8H,C_6H_4]; 4.30(qu), [6H,$OC\underline{H}_2Me$]; 2.50(se), [2H,$C\underline{H}(Me)_2$]; 1.83(s), [6H,p-Me]; 1.29(t), [9H,$OCH_2\underline{Me}$]; 1.15(d), [12H,$CH(\underline{Me})_2$].	95.8(A); 91.3(B); 77.4(C); 75.1(D); 72.4($O\underline{C}H_2Me$); 31.1(E); 22.3(F); 19.7($OCH_2\underline{Me}$); 17.9(G).
$[Ru_2(\mu\text{-OMe})_2(OMe)_2(\eta^6\text{-p-cymene})_2]HBPh_4$ [be]	4.68(AB), [8H,C_6H_4]; 4.06(s), [6H,μ-OMe]; 3.38(s), [6H,OMe]; 2.53(se), [2H,$C\underline{H}(Me)_2$]; 1.90(s), [6H,p-Me]; 1.18(d), [12H,$CH(\underline{Me})_2$].	96.2(A); 92.0(B); 77.3(C); 75.1(D); 67.2(OMe); 31.2(E); 22.3(F); 18.0(G).
$[Ru_2(\mu\text{-OEt})_2(OEt)_2(\eta^6\text{-p-cymene})_2]HBPh_4$ [be]	4.62(AB), [8H,C_6H_4]; 4.30(qu), [4H,μ-$OC\underline{H}_2Me$]; 3.65(qu), [4H,$OC\underline{H}_2Me$]; 2.50(se), [2H,$C\underline{H}(Me)_2$]; 1.80(s), [6H,p-Me]; 1.29(t), [12H,$OCH_2\underline{Me}$]; 1.15(d), [12H,$CH(\underline{Me})_2$].	

(106)

[a] In d^3-$MeNO_2$; [b] Data taken from spectra of mixture (see sec. 3.4) for full discussion. BPh_4 multiplets were observed in the spectra of these mixtures ca δ = 7.7 ppm and 7.3 ppm. [c] OH resonances not observed. [d] In d^6-Me_2CO. [e] In $CDCl_3$.

The mesitylene and p-cymene ring carbons labelled as in the table are assigned as follows.



s = singlet, d = doublet, t = triplet, qu = quartet, se = septet, m = multiplet.

Chapter 4

Syntheses and Electrochemical Studies of Binuclear Ruthenium and Osmium Triple Halo-Bridged Complexes Containing Group 5B Donor Ligands

4.1 Introduction.

In Chapters 2 and 3, the syntheses, spectroscopic characterisation and possible mechanisms of formation of a wide range of binuclear ruthenium(II) and osmium(II) triple bridged complexes containing π-bonded arene rings have been presented. However, as discussed in Chapter 1, these complexes comprise a relatively small proportion of the generic family of compounds $\left[Ru_2(\mu\text{-}X)_3X_nL_{(6-n)}\right]^z$, many of which have been studied in this Department.

In this final chapter, the syntheses and characterisation of some new mixed valence complexes $Ru_2Cl_5Y_n(PR_3)_{4-n}$ (n = 1, Y = CO, CS; PR_3 = PPh_3, P(p-tolyl)$_3$; n = 0, PR_3 = PEt_2Ph) are described, together with electrochemical studies on these and their $Ru_2^{(II,II)}$ precursors, namely $Ru_2Cl_4Y_n(PR_3)_{5-n}$ (n = 0 and 1).

Also, some reactions of $OsCl_2(PPh_3)_3$ with CO, CS_2 and attempted syntheses of new binuclear triple halide bridged complexes of osmium(II) and osmium(II)/ruthenium(II) are discussed.

4.2 Synthesis of some new mixed valence triple-chloro bridged binuclear complexes of ruthenium, containing group 5B donor ligands.

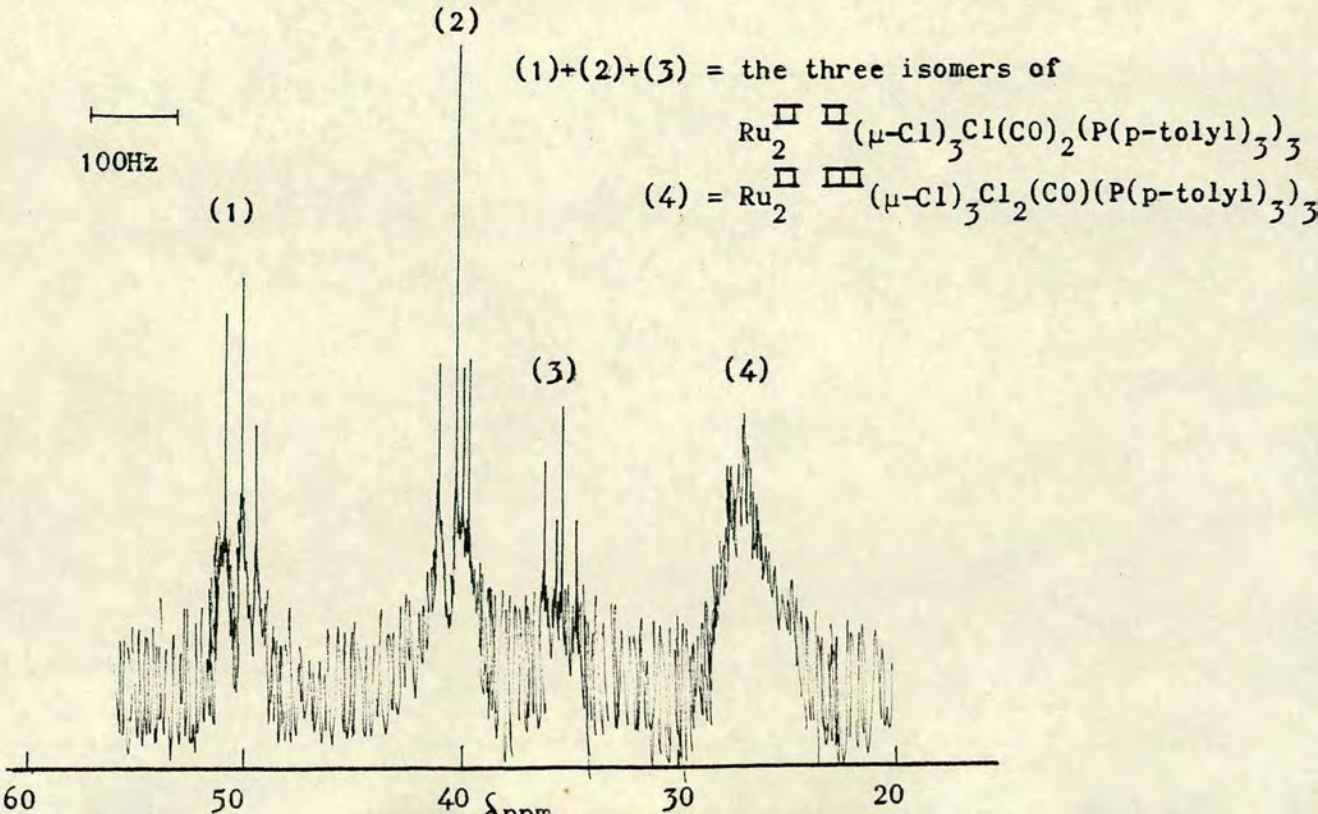
The diruthenium(II) complex $Ru_2(\mu\text{-}Cl)_3Cl(CS)(PPh_3)_4$ was reported to react[92] with concentrated hydrochloric acid in acetone to give the mixed valence $Ru_2^{II,III}$ complex $Ru_2(\mu\text{-}Cl)_3Cl_2(CS)(PPh_3)_3$ (40) and attempts have now been made to extend this reaction to the analogous complexes $Ru_2(\mu\text{-}Cl)_3Cl(Y)(PR_3)_4$ (Y = CO, CS; PR_3 = PPh_3, P(p-tolyl)$_3$).

Thus, the compound $Ru_2(\mu\text{-}Cl)_3Cl(CO)(PPh_3)_4$ was shaken with conc. HCl in acetone for several days(see experimental section 4.5). A slow reaction occurred to give the mixed valence complex $\left[Ru_2^{II,III}-\right.$

$(\mu\text{-Cl})_3Cl_2(CO)(PPh_3)_3]\cdot Me_2CO$. The infra-red spectrum of this compound showed a $\nu(CO)$ vibration at 1970 cm^{-1} as compared to that at 1961 cm^{-1} for the starting complex [89a] and a band at 1700 cm^{-1} corresponding to the $\nu(CO)$ vibration of an acetone of solvation. However, although reaction of $Ru_2(\mu\text{-Cl})_3Cl(CO)(P(p\text{-tolyl})_3)_4$ with conc. HCl in acetone, also gave the desired mixed valence complex $[Ru_2(\mu\text{-Cl})_3Cl_2(CO)(P(p\text{-tolyl})_3)_3]\cdot 2Me_2CO$, on one occasion, the product was shown by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy to be a mixture of this complex and the three geometrical isomers of $Ru_2(\mu\text{-Cl})_3Cl(CO)_2(P(p\text{-tolyl})_3)_3$. Thus, in $CDCl_3$ at 298K, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum consisted of three singlet resonances at δ = 52.1 ppm., 51.2 ppm and 50.5 ppm. respectively and three overlapping AB quartets between δ = 42.0 ppm. and 37.0 ppm. These data correlate well with the published spectrum of the isomeric mixture of $Ru_2(\mu\text{-Cl})_3Cl(CO)_2(P(p\text{-tolyl})_3)_3$.[89b] In addition, a broad resonance is observed at ca δ = 29.3 ppm. which presumably arises from the paramagnetic $Ru_2(\mu\text{-Cl})_3Cl_2CO(P(p\text{-tolyl})_3)_3$ (see Fig. 4.1).

Fig. 4.1.

$^{31}P\text{-}\{^1H\}$ of mixture obtained from the reaction of $Ru_2(\mu\text{-Cl})_3Cl(CO)(P(p\text{-tolyl})_3)_4$ with conc. HCl in acetone.



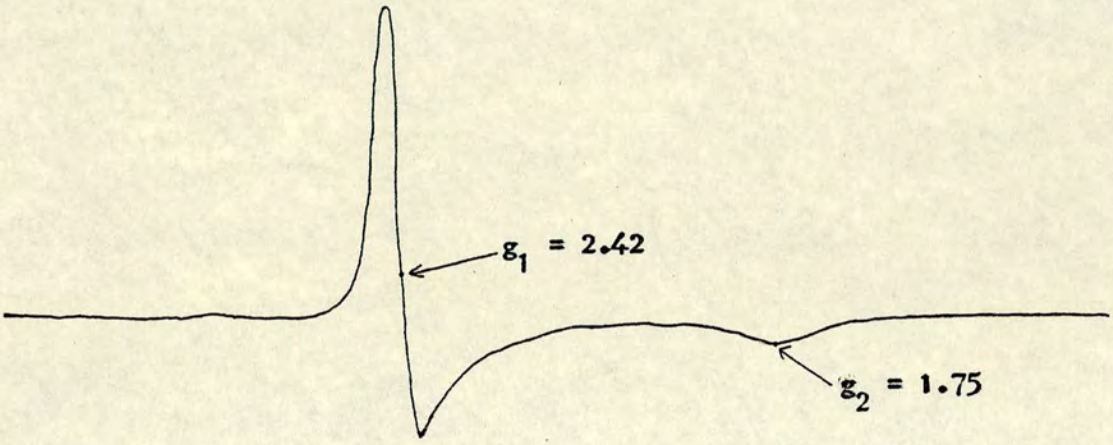
The dicarbonyl compound is probably formed either by carbonyl extraction from acetone or by bridge cleavage and then recombination (with phosphine loss) under the reaction conditions. In order to minimise any competitive decarbonylation and cleavage reactions, several other solvent systems were investigated. In benzene the compound $Ru_2(\mu\text{-}Cl)_3Cl(CO)(PPh_3)_4$ reacted with conc. HCl to give a dirty brown, amorphous powder, which nevertheless gave a ν(CO) vibration at 1976 cm^{-1} in its infra-red spectrum, indicating that the desired product had probably been formed. No reaction appears to occur in either methanol or neat conc. HCl. However, in nitromethane, the reaction with conc. HCl gave a microcrystalline sample of $\left[Ru_2(\mu\text{-}Cl)_3Cl_2(CO)(PPh_3)_3\right].MeNO_2$ (see experimental section 4.5 and Table 4.2). Similarly, the reaction of $Ru_2(\mu\text{-}Cl)_3Cl(CS)(PPh_3)_4$ with conc. HCl in nitromethane gave $\left[Ru_2(\mu\text{-}Cl)_3Cl_2(CS)(PPh_3)_3\right].MeNO_2$. This complex shows one ν(CS) vibration at 1296 cm^{-1} in its infra-red spectrum, as compared to that at 1284 cm^{-1} for the starting complex.[92] The band at 1296 cm^{-1} compares very favourably with the band at 1297 cm^{-1} observed in the previously reported spectrum of this complex made in an acetone/HCl medium.[92] However, an extra band at 1303 cm^{-1} was also found in the ir. spectrum of this sample[92] which may have been due to a small amount of impurity; (NB. For $Ru_2Cl_4(CS)_2(PPh_3)_3$, ν(CS) occurs at 1300 cm^{-1} which suggests that some bridge cleavage and reformation with PPh_3 loss might occur). The e.s.r. spectra of these carbonyl and thiocarbonyl mixed valence complexes reveal a two g value pattern (see experimental section 4.5 and Fig. 4.2 for Y = CO), indicating that the complexes must have a plane of symmetry[134], and therefore configuration (69a) rather than (69b) is proposed.

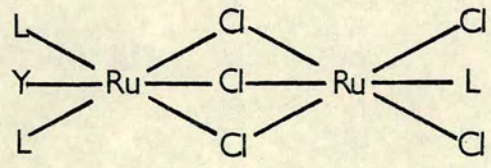
Magnetic measurements on $Ru_2Cl_5(CS)(PPh_3)_3$ (μeff. = 2.0/dimer at 292K) are consistent with the formulation of one unpaired

electron per dimer[92] although no information regarding the location of this electron can be ascertained definitively from either the magnetic or the e.s.r. data.

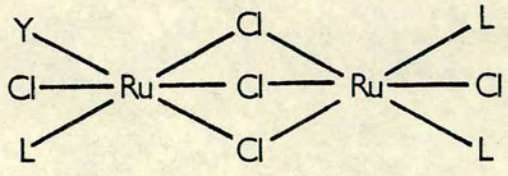
Fig. 4.2.

E.s.r. spectrum at 77K of $[Ru_2(Cl)_3Cl_2(CO)(PPh_3)_3]\cdot MeNO_2$ in CH_2Cl_2.





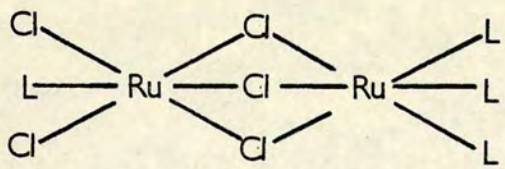
(69a)



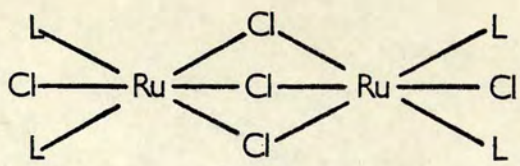
(69b)

(Y = CO, CS; L = PPh_3, P(p-tolyl)$_3$)

The orange/brown complex $Ru_2(\mu\text{-}Cl)_3Cl(PEt_2Ph)_5$ was also found to react with conc. HCl in either acetone or nitromethane to give the green mixed valence complex $Ru_2^{II,III}(\mu\text{-}Cl)_3Cl_2(PEt_2Ph)_4$. The e.s.r. spectrum of this complex also shows a two g value pattern although in this instance, since both configuration (70a) and (70b) possess a plane of symmetry this e.s.r. evidence cannot distinguish between the two possibilities. Hopefully, an X-ray structural determination, which is now in progress, will settle this question unequivocally.



(70a)



(70b)

($L = PEt_2Ph$)

As mentioned earlier (see Chapter 1, section 1.7), the dark red mixed valence complexes $Ru_2(\mu\text{-}Cl)_3Cl_2L_4$ (43) ($L = P^nBu_3$, P^nPen_3) have been synthesised[94] and X-ray analysis[95] has shown that the configuration is of type (70b). However, this was formed under very different conditions (prolonged reaction of "$RuCl_3xH_2O$" with PR_3 in ethanol) and thus, there is no reason to suppose that the reaction of the binuclear complex with HCl will necessarily give the same isomeric form.

The complex $Ru_2(\mu\text{-}Cl)_3Cl_2(PEt_2Ph)_4$ has a magnetic moment of 1.82 per dimer (as determined by the Evans solution method at 298K), indicating the presence of one unpaired electron in the molecule. (cf. $Ru_2Cl_5CS(PPh_3)_3$; μ_{eff} = 2.0/dimer).[92] The $^{31}P\text{-}\{^1H\}$ n.m.r.

spectrum of $Ru_2Cl_5(\mu\text{-}Cl)_3Cl_2(PEt_2Ph)_4$ in $CDCl_3$ at 298K shows a broad hump centred at δ = 44.4 ppm. which is in keeping with the observed paramagnetism of this compound.

It is probable that these reactions all occur via protonation of a co-ordinated tertiary phosphine ligand which is then released as the phosphonium salt; finally, attack of a chloride anion gives the oxidised product although at this juncture, the point at which oxidation occurs is not clear.

Preliminary studies indicate that this mixed valence complex can also be obtained by the reaction of $[Ru_2(\mu\text{-}Cl)_3(PEt_2Ph)_6]Cl$ with conc. HCl in nitromethane. The apparent success of this latter reaction opens up the possibility of generating the corresponding mixed valence complexes containing tertiary phosphite, phosphonite and phosphinite ligands directly from the well-known cationic compounds. This route would be especially valuable for L = $P(OR)R_2$, $P(OR)_2R$ since the neutral complexes $Ru_2(\mu\text{-}Cl)_3ClL_5$ have never been prepared. Several preliminary reactions have been carried out on the tetraphenylborate salts of complexes containing these ligands but as yet no mixed valence compounds have been obtained and only starting materials were recovered. This may be due to the presence of the tetraphenylborate counterion and it may be possible that the reactions will succeed when chloride is the counterion. Alternatively, the Ru-P bonds here may be too inert to undergo protonation under these mild conditions (cf. the inability to form $Ru_2Cl_4L_5$ by pyrolysis of $[Ru_2Cl_3L_6]Cl$ (L = $P(OMe)Ph_2$). Instead, O-R bond rupture occurs to give the unusual neutral dimer $(P(OMe)Ph_2)_2(P(OH)Ph_2)RuCl_3Ru(P(OH)Ph_2)_2(PPh_2O)$ (39).[91]

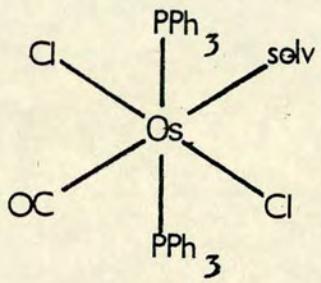
4.3 Synthesis and reactions of $OsCl_2(PPh_3)_3$ and $OsCl_2(CO)(PPh_3)_2(solv)$, (solv. = dmf. MeOH).

Full experimental details for the preparation of the complex $OsCl_2(PPh_3)_3$ were first reported in 1974,[136] namely by reaction of $Na_2[OsCl_6]$ with excess PPh_3 in boiling 95% aqueous ethanol. This reaction was claimed to give $OsCl_2(PPh_3)_3$ in 80% yield, but, when repeated in our laboratories, maximum yields of only ca 20% were recorded (see experimental section 4.5). The $OsCl_2(PPh_3)_3$ precipitated out from solution as a green solid leaving a variety of osmium complexes in solution which at this juncture have not been separated or characterised. A green precipitate of $OsCl_2(PPh_3)_3$ was also obtained in low yield from the reaction in methanol.

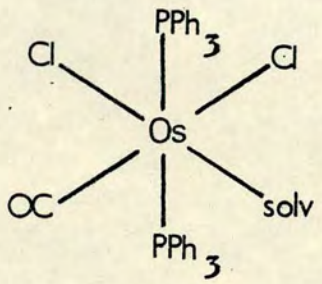
The $^{31}P-\{^1H\}$ n.m.r. spectrum of $OsCl_2(PPh_3)_3$ was recorded at several temperatures in CH_2Cl_2/d^8-toluene (5:1 v/v). Thus, at 298K a single resonance is observed at $\delta = -4.2$ ppm. On cooling, this resonance broadens until at 183K two separate signals are observed as a triplet at -7.4 ppm. and a doublet at -1.7 ppm.($^2J(PP) = 12.2Hz$) of relative intensity 1:2 respectively. This is in good agreement with the $^{31}P-\{^1H\}$ n.m.r. spectrum obtained by Hoffman and Caulton[137] on a sample of $OsCl_2(PPh_3)_3$ made by reacting $(NH_4)_2[OsCl_6]$ with an excess of PPh_3 for 115 hours in a refluxing mixture of ^tBuOH and H_2O.

The reaction of $OsCl_2(PPh_3)_3$ with carbon monoxide in dimethylformamide (dmf) gave a cream coloured product which was characterised as $OsCl_2(CO)(PPh_3)_2$dmf. Thus, the compound exhibits a single resonance at $\delta = 10.3$ ppm. in $CDCl_3$ at 298K in its $^{31}P-\{^1H\}$ n.m.r. spectrum and a single $\nu(CO)$ vibration at 1898 cm^{-1} (nujol mull) as well as that due to a co-ordinated dmf. ligand at 1625 cm^{-1} in its ir. spectrum. This complex could be recrystallised from MeOH/CH_2Cl_2 to give a compound which ir. and $^{31}P-\{^1H\}$ n.m.r. spectroscopy

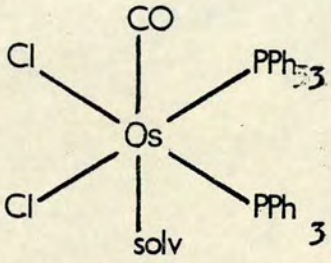
showed to be a mixture of mainly $OsCl_2(CO)(PPh_3)_2(MeOH)$ (δ = 11.1 ppm. ν(CO), 1902 cm^{-1}; ν(C-O)(MeOH), 1020 cm^{-1}) and $OsCl_2(CO)(PPh_3)_2dmf$. in intensity ratio ca 3:1. Both these solvate complexes are thought to have configuration (71a) rather than (71b) or (71c) by analogy with the known ruthenium complexes $RuCl_2Y(PR_3)_2(solv)$. (R = Ph, p-Me-C_6H_4; Y = CO,CS; solv = dmf, MeOH).[89a,89b,92]



(71a)

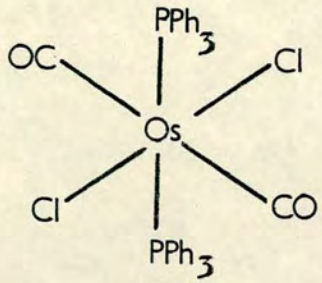


(71b)



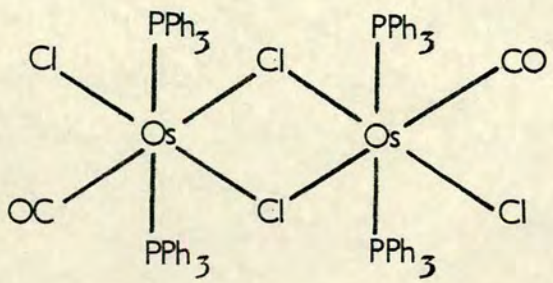
(71c)

An attempt was made to prepare the methanolate complex directly by carbonylation of $OsCl_2(PPh_3)_3$ in methanol. A white solid was obained which $^{31}P-\{^1H\}$ n.m.r. and ir. spectroscopy showed to be a mixture of two compounds. Thus, there are two ^{31}P n.m.r. resonances at 11.2 ppm. and -6.0 ppm. in intensity ratio 2.5:1. The former can be attributed to the compound $OsCl_2(CO)(PPh_3)_2(MeOH)$ and the infra-red spectrum supports this since strong ν(CO) bands are observed at 1902 cm^{-1} and at 1020 cm^{-1} (νCO(MeOH)). There is one other ν(CO) vibration at 1965 cm^{-1} which probably arises from the all trans-dicarbonyl $OsCl_2(CO)_2(PPh_3)_2$ (72).



(72)

In an attempt to synthesise the new complex $Os_2(\mu\text{-}Cl)_3Cl(CO)(PPh_3)_4$, the compounds $OsCl_2(PPh_3)_3$ and $OsCl_2(CO)(PPh_3)_2$dmf. (in a 1:1 molar ratio) were refluxed together in acetone. An orange solid was produced which gave a yellow solution in $CHCl_3$ which slowly turned green on air exposure, presumably because of air oxidation. The $^{31}P\text{-}\{^1H\}$n.m.r. and ir. spectra showed the presence of some unreacted $OsCl_2(CO)(PPh_3)_2$dmf. (δ = 10.1 ppm., ν(CO), 1898 cm^{-1}), a major product with a ^{31}P resonance at 11.3 ppm. and a minor product with a ^{31}P n.m.r. singlet at 0.8 ppm.. As well as the carbonyl band due to the dmf. complex, there is another carbonyl vibration in the infra-red spectrum at 1935 cm^{-1}. Since the carbonyl band has shifted to higher frequency as is observed when $RuCl_2(CO)(PPh_3)_2$dmf. (ν(CO), 1916 cm^{-1}) is reacted with $RuCl_2(PPh_3)_3$ to give $Ru_2(\mu\text{-}Cl)_3Cl(CO)(PPh_3)_4$ (ν(CO), 1961 cm^{-1}), it is possible that the product giving rise to this carbonyl band is dimeric in nature. Since $Os_2Cl_4CO(PPh_3)_4$ has clearly not been formed, (the $^{31}P\text{-}\{^1H\}$n.m.r. spectrum of this should consist of two AB quartets by analogy with that of $Ru_2Cl_4CO(PPh_3)_4$[89a],) the most likely dimer would be the double chloro bridged $[OsCl_2CO(PPh_3)_2]_2$ with configuration (73) or isomers thereof, with the proviso that the PPh_3 groups remain magnetically equivalent (cf. $[RuCl_2CO(PPh_3)_2]_2$ with a ^{31}P resonance at 25.2 ppm.).[89a] This could be formed by dimerisation of the co-ordinatively unsaturated species $OsCl_2CO(PPh_3)_2$, generated in solution by loss of the dmf. molecule under reflux conditions.



(73)

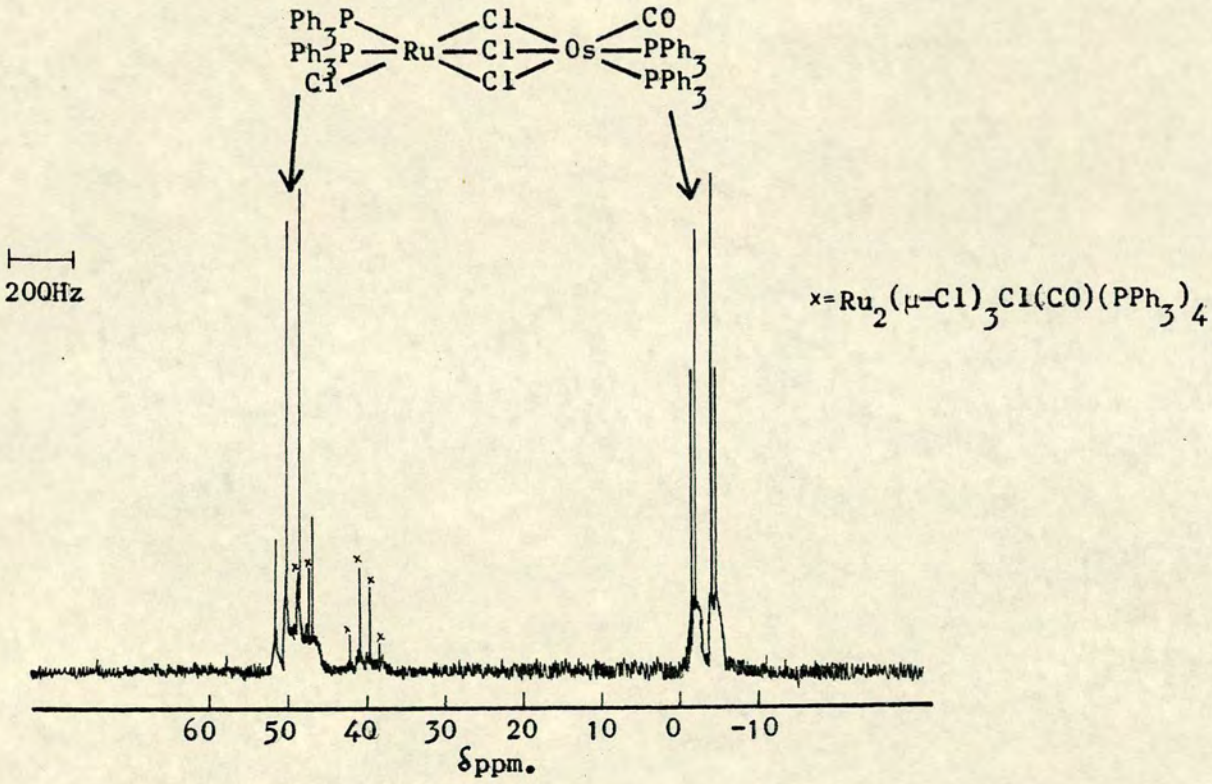
No attempts have been made to separate these compounds as yet and hence further speculation on the structure is unwarranted at this point. A further mystery is that there appears to be no resonance corresponding to unreacted $OsCl_2(PPh_3)_3$. A possible explanation of this is that the dmf. lost from $OsCl_2CO(PPh_3)_2$dmf. might further react with $OsCl_2(PPh_3)_3$(!!). The failure of this reaction to generate the triple-chlorobridged complex $Os_2(\mu\text{-}Cl)_3Cl(CO)(PPh_3)_4$ can be attributed either to the stability of $OsCl_2(PPh_3)_3$ towards dissociation, (cf. $RuCl_2(PPh_3)_3$ where significant amounts of $[RuCl_2(PPh_3)_2]_2$ are formed in solution[87b,137]), and/or to the fact that the dmf. ligand is more strongly bonded to osmium(II) than it is to ruthenium(II). This is a characteristic property of 3rd row compared to 2nd row "d block" metals in the same triad.

The reaction of $RuCl_2(CO)(PPh_3)_2$dmf. with $OsCl_2(PPh_3)_3$ (1:1 molar ratios) in refluxing acetone gave a brown solid which shows a broad ν(CO) band at 1960 cm^{-1} in its ir. spectrum. However, this product was completely insoluble in all common organic solvents and no further studies were attempted. However, the reaction of $RuCl_2(PPh_3)_3$ with an impure sample of $OsCl_2(CO)(PPh_3)_2(MeOH)$ (prepared by carbonylation of $OsCl_2(PPh_3)_3$ in methanol-see above) gave a complex which $^{31}P\text{-}\{^1H\}$n.m.r. and ir. spectroscopic studies strongly indicated to be mainly $(PPh_3)_2(CO)OsCl_3RuCl(PPh_3)_2$ mixed with a small amount of another product. The $^{31}P\text{-}\{^1H\}$n.m.r. in $CDCl_3$ at 298K of the $RuOs(\mu\text{-}Cl)_3Cl(CO)(PPh_3)_4$ complex shows two intense AB quartets centred at δ=49.1 ppm and -2.2 ppm., which can be assigned to the ruthenium and osmium ends of the molecule respectively. (see Fig. 4.3 and experimental section 4.5 for spectral parameters). The complex shows a ν(CO) vibration at 1935 cm^{-1} in its ir. spectrum. The minor product also shows an AB quartet centred at 40.1 ppm.

but unfortunately, the strong AB quartet at 49.0 ppm. masks some of the other resonances which may be associated with this AB pattern. However, the minor product may well be $Ru_2(\mu\text{-}Cl)_3Cl(CO)(PPh_3)_4$ since this is known to have two $^{31}P\text{-}\{^1H\}$ n.m.r. AB resonances centred at 40.0 ppm. and 47.9 ppm..[89a]

Fig. 4.3.

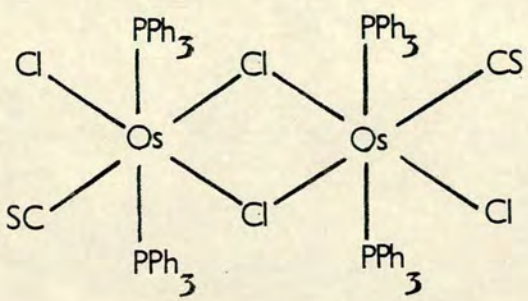
$^{31}P\text{-}\{^1H\}$ n.m.r. spectrum in $CDCl_3$ at 298K of the product from the reaction of $RuCl_2(PPh_3)_3$ with $OsCl_2(CO)(PPh_3)_2(MeOH)$.



It is possible that this compound has been formed either by carbonyl extraction from acetone by $RuCl_2(PPh_3)_3$ to give some $RuCl_2(CO)(PPh_3)_2$-(solv.) which then couples with unreacted $RuCl_2(PPh_3)_3$ to give this product or that it is formed by some interaction with the other osmium carbonyl complex (believed to be $OsCl_2(CO)_2(PPh_3)_2$) present in the sample of $OsCl_2(CO)(PPh_3)_2(MeOH)$.

Finally, the reaction of $OsCl_2(PPh_3)_3$ with CS_2 was examined. Thus, $OsCl_2(PPh_3)_3$ was refluxed in CS_2 for 5 minutes to give a red solution which gave a purple solid on concentration, followed by addition of light petroleum (bp. 60-80°C). The infra-red spectrum of this product showed a strong band at 1287 cm^{-1}, attributable to a ν(CS) vibration. The $^{31}P-\{^1H\}$n.m.r. spectrum in $CDCl_3$ at 298K showed two strong singlets at δ = 43.4 ppm. and 9.3 ppm. and a number of weak signals between 0 ppm. and -12.0 ppm.. The resonance at 43.4 ppm. can be assigned to $SPPh_3$ (reported 42.6 ppm.). By analogy with the reaction of $RuCl_2(PPh_3)_3$ with CS_2, where the double chloro bridged binuclear complex $[RuCl_2(CS)(PPh_3)_2]_2$ was one of the products isolated,[92] the complex giving the ^{31}P n.m.r. resonance at 9.3 ppm. may well be the corresponding osmium complex (74) (cf. $[OsCl_2CO(PPh_3)_2]_2$ with a ^{31}P n.m.r. resonance at 11.3 ppm.). Unlike the $RuCl_2(PPh_3)_3/CS_2$ reaction when the main product is $Ru_2Cl_4CS(PPh_3)_4$[92], no evidence has been found for formation of any $Os_2Cl_4CS(PPh_3)_4$.

In conclusion, it appears that the chemistry of $OsCl_2(PPh_3)_3$ is quite different in some instances to that of its ruthenium analogue. This is not particularly surprising since in solution the two complexes behave quite differently as revealed by $^{31}P-\{^1H\}$n.m.r. spectroscopic measurements. These show that the osmium complex does not dissociate in solution in contrast to the behaviour of the ruthenium compound.



(74)

4.4 Electrochemical studies on some neutral triple chloro-bridged di-ruthenium and osmium/ruthenium compounds.

Introduction

Many triple chloro-bridged binuclear complexes of ruthenium are now known and some of these have recently been studied in our laboratory by electrochemical techniques. Before the results of these studies are discussed further, it is appropriate to give a brief description of these techniques.

Cyclic voltammetry (CV).

Polaragraphy is an electrochemical technique in which changes of current, resulting from the electrolysis of the solution under investigation are followed by varying an applied voltage between a working electrode and a reference electrode, and cyclic voltammetry is one of the more modern developments of this technique. The potential of the working electrode is varied linearly with time at a preset rate, (ν = 20-500 mVs^{-1} is the normal range used), until the required potential is reached and at this point it is brought back to its initial value at the same rate. Typical current-potential curves are shown in Fig. 4.4.

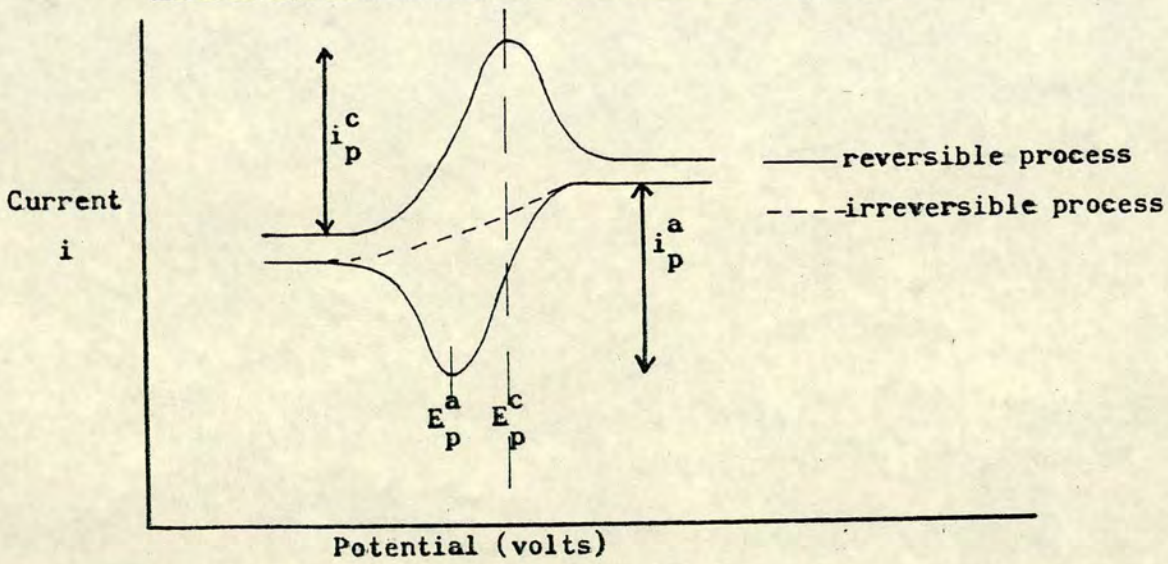
These curves provide four measurable parameters; the net current (i_p^c) and the potential E_p^c at the peak of the cathodic response and the corresponding parameters (i_p^a and E_p^a) for the anodic response. These parameters and that of time can then be used to deduce mechanistic information.

Thus, considering a redox couple, the oxidised form of which is present in solution containing an excess of supporting electrolyte. The role of the supporting electrolyte is to act as the major charge carrier and so diffusion of the reactant from the bulk solution is the only means of mass transport. During a cathodic variation

in potential, the reduced form of the reactant is produced near the electrode. In time this will diffuse into the bulk solution, but if the potential is returned to its initial value at a rate such that some of the reduced form is still present, it can undergo possible oxidation back to the initial couple. If this charge transfer process is much more rapid than the rate of diffusion then it is termed reversible. However, if the reverse is true, it is termed irreversible. The products formed by either oxidation or reduction may decompose and this also leads to irreversibility. A process in which the charge transfer is governed both by diffusion and charge transfer kinetics is termed "quasi-reversible". The criteria for each of these three types of process are tabulated in Table 4.1.

Fig. 4.4.

Cyclic voltammetric current-potential curves.

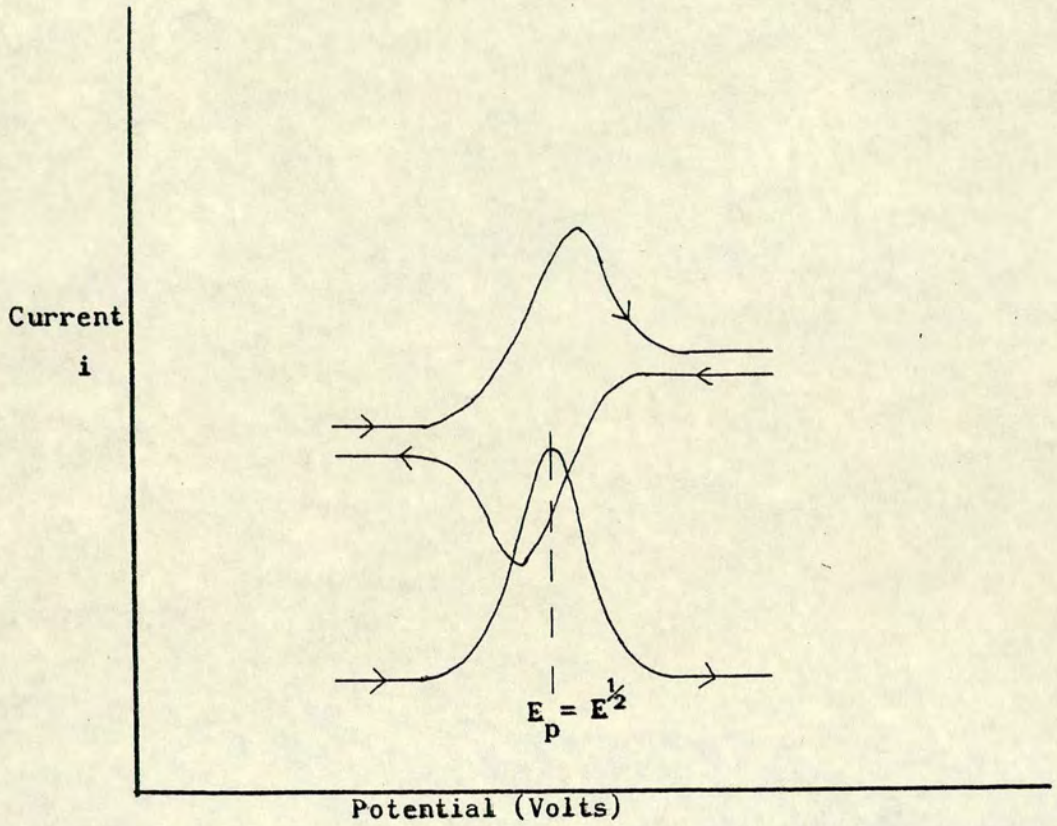


Linear a.c. polarography.

This technique is complimentary to C.V. and involves the superposition of a small alternating potential upon the linearly scanning d.c. potential, resulting in a peaked wave form centred on the classical d.c. wave ie. $E_p = E_{1/2}$ (see Fig. 4.5).

Fig. 4.5.

Polarographic a.c. wave form centred on the d.c. cyclic wave.



An advantage of a.c. polarography is that it can resolve waves which are separated by as little as 40mV and can discriminate against background 'residual' or 'capacitance' currents.

Electrochemical studies on the complexes $Ru_2(\mu\text{-}Cl)_3Cl(Y)(PR_3)_4$ (Y = CO, CS; PR_3 = PPh_3, P(p-tolyl)$_3$.) have recently been reported[139] and these revealed that all these compounds undergo a reversible one-electron oxidation to the corresponding mixed valence cations. $\left[Ru_2(\mu\text{-}Cl)_3ClY(PR_3)_4\right]^{+\cdot}$.* A preliminary controlled electrosynthesis

*Unfortunately, electrochemical studies on binuclear arene complexes of the type described in Chapters 2 and 3 revealed only irreversible redox behaviour, indicating rapid decomposition of the electrogenerated products.

study confirms the indefinite stability of the cation $[Ru_2(\mu\text{-}Cl)_3 Cl(CO)(PPh_3)_4]^+$ at low temperatures (-45°C) but as yet it has not been isolated or characterised further.

Table 4.1.

Criteria for the types of charge transfer processes.

Type	Criteria
Reversible	E_p independent of ν.
	$E_p^c - E_p^a = 59/n$ mV at 25°C and is independent of ν.
	$i_p/\nu^{1/2}$ is independent of ν.
	i_p^a/i_p^c is unity and independent of ν.
Quasi-reversible	E_p shifts with ν.
	$E_p^c - E_p^a$ increases as ν increases.
	$i_p/\nu^{1/2}$ is independent of ν.
	$i_p^a/i_p^c \neq 1$.
Irreversible	E_p shifts with ν.
	$i_p/\nu^{1/2}$ is constant with scan rate.
	There is no current on the reverse scan.

ν = sweep rate in volt sec^{-1}.

n = number of electrons involved in oxidation or reduction process.

The related di-ruthenium(II) complexes $Ru_2(\mu\text{-}Cl)_3ClL_5$ (L = $PClPh_2$, $PMePh_2$, PEt_2Ph) have now been examined electrochemically and shown to undergo a reversible one-electron oxidation in the accessible potential range. The electrode potential is seen to be markedly dependent on the nature of the phosphine (see Table 4.3)

with the more basic phosphines promoting readier oxidation.

The hetero-nuclear complex $(PPh_3)_2(CO)OsCl_3RuCl(PPh_3)_2$ (see section 4.3) also exhibits a fully reversible one-electron oxidation step at +0.80V, which compares well with the potential of +0.75V obtained for the analogous di-ruthenium complex and this suggests that it is the ruthenium end of the heteronuclear complex, which undergoes oxidation. This is consistent with the earlier studies[139] which indicated localised oxidation of the harder $Cl(PR_3)_2Ru$-centre rather than the softer $Y(PR_3)_2Ru$-end. This also lends support to the formulation of the product from the reactions of $Ru_2(\mu\text{-}Cl)_3Cl(Y)(PR_3)_4$ with conc. HCl as being the isomer (a) rather than (b) (see section 4.2) ie. the PR_3 group is preferentially displaced from the harder $Cl(PR_3)_2Ru$-end of the molecule.

The neutral mixed valence complexes $Ru_2(\mu\text{-}Cl)_3Cl_2Y(PR_3)_3$ (Y = CO, CS, PR_3 = PPh_3; Y = CO, PR_3 = P(p-tolyl)$_3$ have also been investigated electrochemically and they all showed a reversible one-electron reduction to the corresponding di-ruthenium (II) monoanion $\left[Ru_2(\mu\text{-}Cl)_3Cl_2Y(PR_3)_3\right]^-$ but no oxidation to the di-ruthenium (III) cations was observed before the onset of multi-electron oxidations at extreme potentials. However, both reversible reduction and reversible oxidation steps were found for the related complex $Ru_2(\mu\text{-}Cl)_3Cl_2(PEt_2Ph)_4$, thus providing the first clear example of the predicted stepwise redox equilibrium(eqn [8]).

$$(RuCl_3Ru)^+ \rightleftharpoons (RuCl_3Ru)^{2+} \rightleftharpoons (RuCl_3Ru)^{3+} \qquad \text{---------- [8] .}$$

EAN 36e 35e 34e

The complex $Ru_2Cl_5(As(p\text{-tolyl})_3)_4$ has recently been synthesised[140] and it also shows both reversible couples; however, their separation

is only 0.73 V compared to the 1.55 V observed for the analogous PEt_2Ph complex. This implies that the more polarisable π-acid tertiary arsine ligand facilitates both oxidation and reduction. The di-ruthenium (III) complex $Ru_2Cl_6(AsPh_3)_3$[139] has been shown to have a single reversible one-electron reduction step forming $[Ru_2Cl_6(AsPh_3)_3]^-$ and it also shows a reversible one-electron oxidation to give a unique 33 electron Ru(III)/Ru(IV) binuclear cation $[Ru_2Cl_6(AsPh_3)_3]^+$ thus extending the sequence of equation [8]. Clearly the structural and spectroscopic changes accompanying these stepwise electron transfers will be of considerable interest, especially since it seems that the degree of metal-metal interaction in 35e and 34e systems may vary in apparently analogous complexes depending on the identity of the terminal ligands eg. $Ru_2^{III,III}Cl_6(AsPh_3)_3$ is magnetically dilute at ambient temperature (μ_{eff} = 1.95/Ru)[139] whereas the remarkable $(PMe_3)_3Ru^{III}(\mu\text{-}CH_2)_3Ru^{III}(PMe_3)_3$ is diamagnetic.[141]

Extensions of this work to a wider range of neutral binuclear ruthenium and osmium complexes are now in progress.

4.5 Experimental

Starting materials.

The compounds $RuCl_2(PPh_3)_3$;[138] $RuCl_2(P(p\text{-tolyl})_3)_3$;[89b] $Ru_2(\mu\text{-}Cl)_3Cl(CO)(PPh_3)_4$;[89a] $Ru_2(\mu\text{-}Cl)_3Cl(CS)(PPh_3)_4$;[92] $Ru_2(\mu\text{-}Cl)_3Cl(CO)(P(p\text{-tolyl})_3)_4$;[89b] $Ru_2(\mu\text{-}Cl)_3Cl(CS)(P(p\text{-tolyl})_3)_4$;[89b] $RuCl_2(CO)(PPh_3)_2$dmf.;[89a] $RuCl_2(CO)(P(p\text{-tolyl})_3)_2$dmf.;[89b] $[Ru_2(\mu\text{-}Cl)_3(PEt_2Ph)_6]Cl$;[83,84] $[Ru_2(\mu\text{-}Cl)_3(P(OMe)Ph_2)_6]BPh_4$;[90] $[Ru_2(\mu\text{-}Cl)_3(PMe_2Ph)_6]BPh_4$[88] and $Ru_2(\mu\text{-}Cl)_3Cl(PEt_2Ph)_5$[86,87b], were prepared by standard literature methods.

Chemicals

As for sections 2.7 and 3.6, plus dimethylformamide and carbon disulphide (Fisons).

Experimental

As for sections 2.7 and 3.6 and electrochemical measurements were made with a three electrode Princeton Applied Research (PAR) model 170 instrument on ca 3×10^{-3} mol dm^{-3} solutions. The triple bridged complexes were dissolved in degassed dichloromethane with supporting electrolyte $[^{n}Bu_4N][BF_4]$ (0.10 mol dm^{-3}). For cyclic voltammetry, potentials were measured at a stationary Pt electrode with reference to a Ag/AgI electrode and scan speeds varied from 20 to 500mV sec^{-1}. The potentials for ac. polarography were measured at a dropping mercury electrode with reference to a Ag/AgI electrode at a scan speed of 20mV sec^{-1}. $^{31}P-\{^{1}H\}$ n.m.r. spectra were recorded on a Jeol FX60 spectrometer operating at 24.21MHz and ^{31}P shifts are quoted w.r.t. 80% H_3PO_4 with positive shifts to higher frequency. E.s.r. measurements were performed on a Hilger and Watts "Microspin" spectrometer operated at 9.33 GHz and employing 100kHz magnetic field modulation and phase sensitive detection. The magnetic field was measured by means of a proton resonance meter and g factors were calculated by using a dilute polycrystalline sample of 1,1-diphenyl-2-picryl-hydrazyl (g = 2.0036) as reference.

Tri-μ-chloro-a-carbonyl-ih-di(chloro)-tris(triphenylphosphine) diruthenium(II,III)(solvate).

Method A. (solvate = acetone) The compound $Ru_2(\mu\text{-}Cl)_3Cl(CO)(PPh_3)_4$ (0.14g, 0.10 mmol) was finely ground and then shaken in acetone (20 cm^3) with conc. HCl (3 cm^3) for four days. An orange brown solid was formed and this was filtered off and washed with water, acetone and

diethylether. Yield 91%; m.p. = 229-230°C ; ν(CO), 1970 cm^{-1}; ν(CO), ('acetone'), 1716 cm^{-1}.

Method B. (solvate = nitromethane). The compound $Ru_2(\mu\text{-}Cl)_3Cl(CO)(PPh_3)_4$ (0.07g, 0.05 mmol) was shaken in $MeNO_2$ (5 cm^3) with conc. HCl (5 cm^3) for four days. A light brown, crystalline solid formed and this was treated as for method A, Yield 63%; m.p. = 228-230°C; ν(CO), 1976 cm^{-1}; ν(NO), 1545 cm^{-1}; e.s.r.:- g_1 = 2.42; g_2 = 1.75.

Tri-μ-chloro-ab-di(chloro)-i-thiocarbonyltris(triphenylphosphine) diruthenium(II)(III)nitromethane.

The compound $Ru_2(\mu\text{-}Cl)_3Cl(CS)(PPh_3)_4$ (0.14g, 0.10 mmol) was shaken in $MeNO_2$ (5 cm^3) with conc. HCl (5 cm^3) for three days. An orange solid was formed and this was filtered off and washed with water, methanol and diethylether. Yield 85%; m.p. = 227-229°C ; ν(CS),1296 cm^{-1}; ν(NO),1545 cm^{-1}; e.s.r:- g_1 = 2.43; g_2 = 1.77.

Tri-μ-chloro-di(chloro)tetrakis(diethylphenylphosphine)diruthenium(II) (III)(solvate).

Method A. (solvate = nitromethane) The compound $Ru_2(\mu\text{-}Cl)_3Cl(PEt_2Ph)_5$ (0.17g, 0.10 mmol) was shaken in $MeNO_2$ (5 cm^3) with conc. HCl (5 cm^3) for three days. A green microcrystalline solid was formed and this was filtered off and washed with water and n-hexane, Yield 30%; m.p.* = 152-154°C (decomp); ν(NO), 1545 cm^{-1}; e.s.r.:- g_1 = 2.46; g_2 = 1.63.

Method B. (solvate = nitromethane). The compound $[Ru_2(\mu\text{-}Cl)_3(PEt_2Ph)_6]Cl$ (0.13g, 0.10 mmol) was shaken in $MeNO_2$ (5 cm^3) with conc. HCl (5 cm^3) for four days. A green solid formed and this was collected as for method A. Yield 24%.

---

*Compounds darken at this temperature, but a clean melt is obtained at 218°-220°C.

Method C. The compound $Ru_2(\mu\text{-}Cl)_3Cl(PEt_2Ph)_5$ (0.10g) was finely ground and shaken in acetone (20 cm^3) with conc. HCl (10 cm^3) for two days. The green precipitate that formed was collected and washed as in methods A and B. m.p.* = 159-161°C(decomp); magnetic moment at 303K = 1.82 per dimer (Evans' method).

Tri-μ-chloro-a-carbonyl-ih-di(chloro)-tris(tri-p-tolylphosphine) diruthenium(II)(III)acetone.

The compound $Ru_2(\mu\text{-}Cl)_3Cl(CO)(P(p\text{-tolyl})_3)_4$ (0.16g, 0.10 mmol) was finely ground and shaken in acetone (30 cm^3) with conc. HCl (3 cm^3) for four days. The orange precipitate was filtered off and washed with water, acetone and diethylether. Yield 71%; ν(CO), 1980 cm^{-1}; ν(CO)('acetone'), 1700 cm^{-1}.

Dichlorotris(triphenylphosphine)osmium(II).

Method A. The compound $Na_2[OsCl_6]$ (1.30g; 3.00 mmol) was added to a refluxing solution of PPh_3 (4.50g, 18 mmol) in ethanol (150 cm^3) After two hours, a green precipitate had formed and the reaction mixture was then filtered hot and the precipitate washed with water, ethanol and pet. ether (b.p. 60-80°C). Yield, 20%; m.p. = 139-141°C $^{31}P\text{-}\{^1H\}$ 298K - 4.2(s) ppm.; 183K - 1.7(d) ppm. - 7.4(t) ppm., $^2J(P\text{-}P)$ = 12.2 Hz.

Method B. The compound $Na_2[OsCl_6]$ (1.30g was added to a refluxing solution of PPh_3 (4.50g) in methanol (100 cm^3) and resulting yellow solution was refluxed for four hours. The solution was cooled and the excess PPh_3 deposited was filtered off. The filtrate was refluxed for a further two hours and a dark green precipitate was formed. This was filtered off and washed with water, methanol and diethylether. Yield, 18%; m.p. = 138-140°C.

Carbonyldi(chloro)(N,N-dimethylformamide)bis(triphenylphosphine) osmium(II).

The compound $OsCl_2(PPh_3)_3$ (0.21g, 0.20 mmol) was suspended in dmf. (6 cm^3) and CO was bubbled through the solution for 10 minutes to give a creamy white precipitate. This was filtered off and washed with diethylether. Yield, 62%; m.p. = 209-211°C; ν(CO), 1898 cm^{-1}; ν(Os-Cl), 300 cm^{-1}; ν(CO)(dmf), 1625 cm^{-1}; $^{31}P-\{^1H\}$ n.m.r. in $CDCl_3$ at 298K, 10.3(s) ppm..

Carbonyldi(chloro)(methanol)bis(triphenylphosphine)osmium(II).

The compound $OsCl_2(CO)(PPh_3)_2$dmf. was recrystallised from methanol/ dichloromethane. ν(CO), 1900 cm^{-1}; (Os-Cl), 310 cm^{-1}, ν(CO)(methanol), 1020 cm^{-1}; $^{31}P-\{^1H\}$ n.m.r. in $CDCl_3$ 11.1(s) ppm.. This product still contained some $OsCl_2CO(PPh_3)_2$dmf. ($^{31}P-\{^1H\}$ n.m.r. evidence).

Tri-μ-chloro-a-chloro-g-carbonyltetrakis(triphenylphosphine)ruthenium(II) osmium(II)acetone.

The compounds $RuCl_2(PPh_3)_3$ (0.09g, 0.10 mmol) and $OsCl_2(CO)(PPh_3)_2$ MeOH (0.08g, 0.10 mmol) were refluxed together in acetone for six hours. The orange precipitate which formed was filtered off and washed with acetone and diethylether. Yield, 73%; ν(CO), 1935 cm^{-1} ν(CO)(acetone), 1700 cm^{-1}; $^{31}P-\{^1H\}$ n.m.r. in $CDCl_3$ at 298°K (see Fig. 4.3) 49.0 (RuP) (qu); -2.2(OsP)(qu) $J(P^1P^2)$ = 39.1Hz, $J(P^3P^4)$ = 12.2Hz, $\delta(P^1P^2)$ = 68.5 Hz, $\delta(P^3P^4)$ = 60.4 Hz. Each peak in the two main quartets shows a further splitting of 2.4 Hz which can probably be attributed to long range coupling of PPh_3 groups across the $-RuCl_3Os-$ bridging unit.

As shown in Fig. 4.3, a small amount of $Ru_2Cl_4CO(PPh_3)_4$ is also formed.

Table 4.2.

Analytical and infra-red data for some new ruthenium and osmium complexes.

Compound	Found %				Calculated %				ν(M-Cl)	Others
	C	H	N	Cl	C	H	N	Cl		
$[Ru_2(\mu\text{-}Cl)_3Cl_2(CO)(PPh_3)_3].Me_2CO$	55.6	4.1	-	-	55.6	4.1	-	-	330(s)cm^{-1},280(m)cm^{-1}	ν(CO) = 1970 cm^{-1}
$[Ru_2(\mu\text{-}Cl)_3Cl_2(CO)(PPh_3)_3].MeNO_2$	52.6	3.8	1.1	14.1	52.6	3.9	1.1	14.1	330(s)cm^{-1},280(m)cm^{-1}	ν(CO) = 1976 cm^{-1}
$[Ru_2(\mu\text{-}Cl)_3Cl_2(CS)(PPh_3)_3].MeNO_2$	52.4	3.9	1.2	13.7	52.9	3.8	1.1	13.9	330(s)cm^{-1},280(m)cm^{-1}	ν(CS) = 1296 cm^{-1}
$[Ru_2(\mu\text{-}Cl)_3Cl_2(CO)(P(p\text{-}tolyl)_3)_3].2Me_2CO$	58.1	4.8	-	-	58.2	4.8	-	-	330(br)cm^{-1},280(w)cm^{-1}	ν(CO) = 1980 cm^{-1}
$Ru_2(\mu\text{-}Cl)_3Cl_2(PEt_2Ph)_4$	46.7	5.8	-	-	46.9	5.9	-	-	[a]325(s)cm^{-1},310(sh)cm^{-1} 235(w)cm^{-1}	--------
$[Ru_2(\mu\text{-}Cl)_3Cl_2(PEt_2Ph)_4].MeNO_2$	44.3	5.8	1.3	15.8	44.6	5.8	1.3	16.0	330(s)cm^{-1},310(sh)cm^{-1}	--------
$OsCl_2(PPh_3)_3$	61.7	4.4	-	-	61.9	4.3	-	-	290 cm^{-1}	--------
$OsCl_2(CO)(PPh_3)_2$dmf.	53.9	4.3	2.0	-	54.1	4.2	1.6	-	300 cm^{-1}	ν(CO) = 1896 cm^{-1}

[a] Spectrum recorded in pressed polyethylene disc.

s = strong, m = medium, w = weak, sh = shoulder, br = broad.

Table 4.3.

Reversible electrode potentials for some binuclear ruthenium and ruthenium/osmium complexes.

Compound	$E_{\frac{1}{2}}$(volts) at 20°C in CH_2Cl_2/0.5M $[^nBu_4N][BF_4]$ [a].		
	(II,II)/(II,III)	(II,III)/(III,III)	(III,III)/(III,IV)
$Ru_2(\mu\text{-}Cl)_3Cl(CO)(PPh_3)_4$	+0.75	-------	-------
$Ru_2(\mu\text{-}Cl)_3Cl(CS)(PPh_3)_4$	+0.74	-------	-------
$Ru_2(\mu\text{-}Cl)_3Cl(CO)(P(p\text{-tolyl})_3)_4$	+0.65	-------	-------
$Ru_2(\mu\text{-}Cl)_3Cl(CS)(P(p\text{-tolyl})_3)_4$	+0.64	-------	-------
$RuOs(\mu\text{-}Cl)_3Cl(CO)(PPh_3)_4$	+0.80	-------	-------
$Ru_2(\mu\text{-}Cl)_3Cl(PClPh_2)_5$	+1.20	-------	-------
$Ru_2(\mu\text{-}Cl)_3Cl(PMePh_2)_5$	+0.75	-------	-------
$Ru_2(\mu\text{-}Cl)_3Cl(PEt_2Ph)_5$	+0.47	-------	-------
$Ru_2(\mu\text{-}Cl)_3(Cl)_2(CO)(PPh_3)_3$	+0.03	-------	-------
$Ru_2(\mu\text{-}Cl)_3Cl_2(CS)(PPh_3)_3$	+0.02	-------	-------
$Ru_2(\mu\text{-}Cl)_3Cl_2(CO)(P(p\text{-tolyl})_3)_3$	-0.06	-------	-------
$Ru_2(\mu\text{-}Cl)_3Cl_2(PEt_2Ph)_4$	-0.28	+1.27	-------
$Ru_2(\mu\text{-}Cl)_3Cl_2(As(p\text{-tolyl})_3)_4$	+0.10	+0.83	-------
$Ru_2(\mu\text{-}Cl)_3Cl_3(AsPh_3)_3$	------	-0.37	+0.67

[a] All potentials are referred to a Ag/AgI/0.5M Bu_4NBF_4/CH_2Cl_2 reference electrode at which ferrocene is oxidised at +0.60V.

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Abbreviations.

Me = methyl

Et = ethyl

Ph = phenyl

Bu = butyl

pent = pentyl

Pr = propyl

thf = tetrahydrofuran

dmf = dimethylformamide

cod = 1,5-cyclooctadiene

py = pyridine

bipy = 1,1 -bipyridyl

m.p. melting point

List of Courses Attended.

1. Why Chemists Use Neutrons. (3 day course at Edinburgh University)
2. Optical Properties of Transition Metal Complexes. (by Dr. T. A. Stephenson).
3. Sulphur Compounds in Organic Syntheses. (by Dr. Leaver.)
4. History of the Chemistry Department. (by Dr. Doyle.)
5. Multiple Resonance n.m.r.. (by B. McFarlane.)
6. Departmental Seminars. (Inorganic.)

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Cationic, Neutral and Anionic Complexes of Ruthenium(II) containing η^6-Arene Ligands

D.R. Robertson, T.A. Stephenson* and (in part) T. Arthur, Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ (Great Britain)

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Summary

Reaction of $[\{Ru(C_6H_6)Cl_2\}_2]$ with an excess of CsCl/HCl in ethanol gives the first anionic arene complex of ruthenium $Cs[Ru(C_6H_6)Cl_3]$ (II) although in aqueous solution this readily loses a chloride ion to give $[Ru(C_6H_6)Cl_2(H_2O)]$ and reactions with various Lewis bases give the compounds $[Ru(C_6H_6)Cl_2L]$ (L = C_5H_5N, Me_2SO, PR_3 etc). Reaction of $[\{Ru(C_6H_6)Cl_2\}_2]$ with NH_4PF_6 in methanol gives high yields of the triple chloride bridged complex $[Ru_2(C_6H_6)_2Cl_3]PF_6$ (III) which, although stable in $MeNO_2$, readily undergoes bridge cleavage reactions in water and Me_2SO. Reaction of (III) with various Lewis bases produces the new monomeric, ruthenium(II), arene cations $[Ru(C_6H_6)ClL_2]PF_6$ (L = C_5H_5N, Et_2S, $AsPh_3$, PR_3 etc).

Introduction

In recent years, some reactions of the unusual η^6-arene complexes $[\{Ru(arene)X_2\}_2]$ (arene = C_6H_6, C_6H_5OMe, p- and m-$C_6H_4Me_2$, C_6H_5Me, 1,3,5-$C_6H_3Me_3$, p-$MeC_6H_4CHMe_2$; X = Cl or Br) have been investigated by several workers [1-7]. In particular, bridge cleavage reactions with a variety of Lewis bases to give the neutral, monomeric complexes $[Ru(arene)X_2L]$ (L = PR_3, $P(OR)_3$, AsR_3, C_5H_5N etc) are well documented [1-3].

In this paper, we now report the full results [8] of the formation of the benzene anion $[Ru(C_6H_6)Cl_3]^-$ and the triple chloride bridged cation $[C_6H_6RuCl_3RuC_6H_6]^+$ from $[\{Ru(C_6H_6)Cl_2\}_2]$, together with details of the reactions of these compounds with various Lewis bases.

Results and Discussion

a) Synthesis and reactions of $Cs[Ru(C_6H_6)Cl_3]$

As reported earlier [9], reaction of the compound $[\{Ru(CO)Cl_2(C_7H_8)\}_2]$ (C_7H_8 = bicyclo [2.2.1] hepta-2,5-diene) with MCl/HCl (M = $Ph_3(PhCH_2)P^+$, Cs^+) in degassed acetone gave a high yield of the first anionic diene complex of ruthenium $M[Ru(CO)Cl_3(C_7H_8)]$. An attempt has now been made to synthesise the first anionic η^6-arene ruthenium complex using a similar preparative route. Thus, shaking $[\{Ru(C_6H_6)Cl_2\}_2]$ (I) with a mixture of excess CsCl and concentrated HCl in ethanol for several days gave an orange powder analysing closely for $Cs[Ru(C_6H_6)Cl_3]$ (II) although it was always difficult to obtain this complex completely free of CsCl. The mull i.r. spectrum of (II) indicated the presence of coordinated benzene and contained a broad band at 280 cm^{-1} assigned to terminal ν(RuCl) stretching vibration(s). Since compound (II) posesses C_{3v} symmetry, two ν(RuCl) bands were expected and thus, the broad band at 280 cm^{-1} might contain both the a_1 and e vibrational modes or a weak band at 298 cm^{-1} could be assigned to one of the ν(RuCl) bands. Unfortunately, attempts to make the corresponding $[Ru(C_6H_6)X_3]^-$ ($X = Br^-$, I^-) anions, either by reaction of $[\{Ru(C_6H_6)X_2\}_2]$ or $Cs[Ru(C_6H_6)Cl_3]$ with X^- were unsuccessful, only $[\{Ru(C_6H_6)X_2\}_2]$ being recovered from the reaction mixture in each case.

As expected, $Cs[Ru(C_6H_6)Cl_3]$ was more soluble in water than $[\{Ru(C_6H_6)Cl_2\}_2]$ and an aqueous solution of (II) was highly conducting (eg. for a 10^{-3} mol dm^{-3} solution, Λ_m = 374 S cm^2 mol^{-1}). Unfortunately the unavoidable presence of a small amount of CsCl, together with the fact that ^1H nmr studies on (II) in aqueous solution indicated that extensive dissociation of chloride ion occurred meant that no firm conclusion about

electrolyte type could be drawn from these conductivity measurements.

The ^{1}H nmr spectrum of $Cs[Ru(C_6H_6)Cl_3]$ in D_2O consisted of a single η^6-C_6H_6 resonance at 6.40δ whereas that of $[\{Ru(C_6H_6)Cl_2\}_2]$ in D_2O showed two coordinated benzene resonances at 6.39(vs) and 6.50(w)δ which previous workers have assigned to either the aqua complexes $[Ru(C_6H_6)Cl(D_2O)_2]^+$ and $[Ru(C_6H_6)(D_2O)_3]^{2+}$ respectively or to a combination of one of these cations and the neutral complex $[Ru(C_6H_6)Cl_2D_2O]$[1].* It is therefore very likely that the signal at 6.40δ observed for (II) in D_2O is due to an aqua complex formed by displacement of chloride ion, and by reference to the reactions of (II) with Lewis bases, (see below), this aqua complex is probably the neutral $[Ru(C_6H_6)Cl_2(D_2O)]$. In an attempt to suppress this dissociation process and obtain the ^{1}H nmr spectrum of (II), large amounts of CsCl/HCl were added to the D_2O solution of (II). Unfortunately, the residual water peak became more intense and shifted to higher frequencies (from 5.20 to 5.90δ), thus obscuring any new η^6-C_6H_6 resonance, and furthermore, slow precipitation of $[\{Ru(C_6H_6)Cl_2\}_2]$ also occurred.

Earlier, $Ph_3(PhCH_2)P[Ru(CO)Cl_3(C_7H_8)]$ was shown to be a good precursor for synthesising a wide range of anionic complexes of the type $Ph_3PhCH_2P[Ru(CO)Cl_3L_2]$ (L = $AsPh_3$, C_5H_5N, Me_2S etc) via displacement of diene [10]. Attempts, however, to synthesise the unknown fac-$[RuCl_3L_3]^-$ anions by reaction of $Cs[Ru(C_6H_6)Cl_3]$ with excess of various

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* Zelonka and Baird [1] quoted the resonance positions for $[\{Ru(C_6H_6)Cl_2\}_2]$ in D_2O at 5.93 and 6.03δ. The discrepancy between their work and the chemical shifts given above probably arises from the fact that these chemical shifts are relative to an external TMS capillary whereas in ref [1] they are with respect to an internal TMS lock. Support for this explanation comes from the shift to high frequency observed for the co-ordinated η^6-C_6H_6 resonance in the ^{1}H nmr spectrum of $[Ru(C_6H_6)Cl_2(PMe_2Ph)]$ when run in $CDCl_6$ with respect to an external TMS capillary (5.95δ) as opposed to an internal TMS reference (5.35δ). Also, the difference between the chemical shifts of the two η^6-C_6H_6 resonances of $[\{Ru(C_6H_6)$-$Cl_2\}_2]$ in D_2O is very similar with respect to both the external TMS reference (0.11δ) and the internal TMS lock (0.10δ).

L gave only neutral complexes. Thus, either shaking or gently refluxing (II) with excess of pyridine in methanol gave a yellow solution, and the orange solid isolated from this by concentration followed by precipitation with diethyl ether analysed very closely for $[Ru(C_6H_6)Cl_2(C_5H_5N)]$. The compound was insoluble in most deuterated solvents except d^6-Me_2SO and its ^1H nmr spectrum in this solvent showed broad resonances at ca. 7.3 and 8.3δ (C_5H_5N) plus two η^6-C_6H_6 resonances at 5.65 and 5.90δ. The latter was assigned to the d^6-Me_2SO complex $[Ru(C_6H_6)Cl_2(d^6\text{-}Me_2SO)]$, (reported in ref [1] to have an η^6-C_6H_6 ^1H nmr resonance at 5.93δ) and this was verified by synthesising $[Ru(C_6H_6)Cl_2(Me_2SO)]$, either by refluxing $[Ru(C_6H_6)Cl_2(C_5H_5N)]$ or $Cs[Ru(C_6H_6)Cl_3]$ with excess Me_2SO in methanol. In contrast, prolonged refluxing of (II) in neat pyridine gave a mixture of $[Ru(C_6H_6)Cl_2(C_5H_5N)]$ and the well-known [11] trans-$[RuCl_2(C_5H_5N)_4]$.

The products from the reaction of compound (II) and tertiary phosphines were dependent both on the reaction conditions and the nature of the phosphine. Thus, if (II) was shaken with excess PR_3 in methanol (PR_3 = PPh_3, PMe_2Ph, $PMePh_2$) the previously reported [1-3] monomeric complexes $[Ru(C_6H_6)Cl_2(PR_3)]$ were formed. Similarly, $[Ru(C_6H_6)Cl_2(SbPh_3)]$ was prepared by shaking (II) and excess $SbPh_3$ in methanol. However, under reflux conditions, the reaction with tertiary phosphines resulted in loss of the benzene ring from $Cs[Ru(C_6H_6)Cl_3]$. For example, refluxing (II) with excess of PMe_2Ph in methanol gave cis-$[RuCl_2(PMe_2Ph)_4]$, previously synthesised either by reaction of excess PMe_2Ph with $[RuCl_2(PPh_3)_3]$ in degassed light petroleum (bp 60 - 80°C) or with mer-$[RuCl_3(PMe_2Ph)_3]$ in hexane [12]. In CH_2Cl_2, cis-$[RuCl_2(PMe_2Ph)_4]$ readily rearranged to $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ [12]. In contrast, refluxing (II) with excess PPh_3 in methanol gave $[RuCl_2(PPh_3)_3]$, previously prepared by refluxing "$RuCl_3xH_2O$" with excess of PPh_3 in methanol [13].

Hence, although the complex $Cs[Ru(C_6H_6)Cl_3]$ is in itself of interest in so much as it represents the first anionic arene complex of ruthenium,

the lability of the coordinated benzene group is very much less than that of the diene in $[Ru(CO)Cl_3(C_7H_8)]^-$. Thus, loss of chloride ion from $[Ru(C_6H_6)Cl_3]^-$ occurs much more readily than loss of the C_6H_6 ring and therefore, little is to be gained by using the $[Ru(C_6H_6)Cl_3]^-$ anion rather than $[\{Ru(C_6H_6)Cl_2\}_2]$ as a starting material.

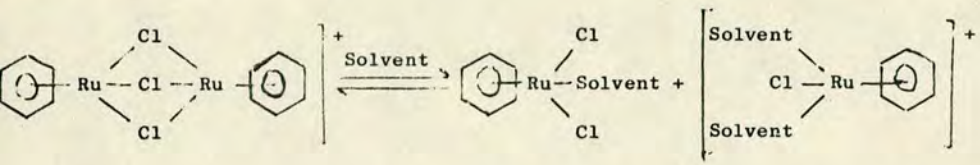
b) Synthesis of $[C_6H_6RuCl_3RuC_6H_6]PF_6$

As reported earlier by Bennett and Smith [3], the reaction of $[\{Ru(C_6H_6)Cl_2\}_2]$ (I) with hot water gave an orange solution from which NH_4PF_6 slowly precipitated in ca 40% yield, an orange solid identified as $[Ru_2(C_6H_6)_2Cl_3]PF_6$ (IIIa). In our hands, however, this reaction produced only low variable yields (ca. 12%) of (IIIa) plus, on one occasion, a further product (see experimental section) shown by X-ray analysis [14] to be $[Ru(NH_3)_2(C_6H_6)Cl]_3(PF_6)_3NH_4PF_6$. Since the $[Ru_2(C_6H_6)_2Cl_3]^+$ cation is isoelectronic with $[Rh_2Cl_3(C_5Me_5)_2]^+$, which was isolated in high yield from reaction of $[\{RhCl_2(C_5Me_5)\}_2]$ with $NaBPh_4$ in methanol [15], a similar preparative route for (III) has been examined. Thus, stirring the dark red-brown $[\{Ru(C_6H_6)Cl_2\}_2]$ in methanol at ambient temperature with a slight excess of NH_4PF_6 for 24h gave, in high yield, (> 90%) a dark orange-yellow solid which analysed quite well for $[Ru_2(C_6H_6)_2Cl_3]PF_6$ (IIIb). No apparent reaction occurred in the absence of NH_4PF_6 or if methanol was replaced by acetone.

The mull ir spectrum of (IIIb) confirmed the presence of PF_6^- and in the far ir spectrum two intense bands at 276, 264 cm^{-1} were observed, indicative of bridging ν(RuCl) vibrations (cf in ref [3], ν(RuCl) of (IIIa) quoted at 265 cm^{-1}). Compound (IIIb) gave conducting solutions in $MeNO_2$ with values characteristic of 1:1 electrolytes [16] (eg. for a 10^{-3} mol dm^{-3} solution, Λ_m = 82 S cm^2 mol^{-1}) and this was supported by $\Lambda_o - \Lambda_c$ vs $C^{\frac{1}{2}}$ plots over a range of concentrations which had a slope characteristic of 1:1 electrolytes (see experimental section). The ^1H and $^{13}C-\{^1H\}$ nmr spectra of (IIIb) in d^3-$MeNO_2$ at ambient

emperature both showed a single sharp resonance for the η^6-C_6H_6 groups
t 5.90δ and 82.0 ppm respectively, indicating that the dimeric unit
emained intact in this solvent.

However, in other solvents such as D_2O and d^6-Me_2SO, more than one
^{6}-C_6H_6 resonance was observed. Thus, the ^{1}H nmr spectrum of (IIIa or b)
n D_2O contained <u>two</u> η^6-C_6H_6 resonances at 6.35 and 6.48δ[†] of <u>comparable
ntensity</u>. These resonance positions are virtually identical to those
ound for $[\{Ru(C_6H_6)Cl_2\}_2]$ dissolved in D_2O [6.39 and 6.50δ - see
ection a)] indicating facile bridge cleavage has occurred as shown in
he equation.



In d^6-Me_2SO, three singlets were observed in the ^{1}H nmr spectrum
f (IIIb) at 5.95(vs), 6.15(w) and 6.50(s)δ which corresponded closely
o the quoted positions of the η^6-C_6H_6 resonances for the species [Ru-
$C_6H_6)Cl_2(d^6$-$Me_2SO)]$ (5.93δ), $[Ru(C_6H_6)Cl(d^6$-$Me_2SO)_2]^+$ (6.12δ) and
$Ru(C_6H_6)(d^6$-$Me_2SO)_3]^{2+}$ (6.47δ) [1]. The relative intensities of these
ignals suggested that the monocation has reacted further with d^6-Me_2SO
o give the dication.

As discussed elsewhere [17] for the closely related $[Ru_2Cl_3L_6]^+$
ations, (L = PR_3, $P(OR)Ph_2$, $P(OR)_2Ph$), the most likely mechanism of
ormation of $[Ru_2(C_6H_6)_2Cl_3]^+$ is by intermolecular coupling of the
eakly solvated monomers $[Ru(C_6H_6)Cl_2(solvent)]$ and $[Ru(C_6H_6)Cl(solvent)_2]^+$,
he monomers being formed by reaction of $[\{Ru(C_6H_6)Cl_2\}_2]$ with either

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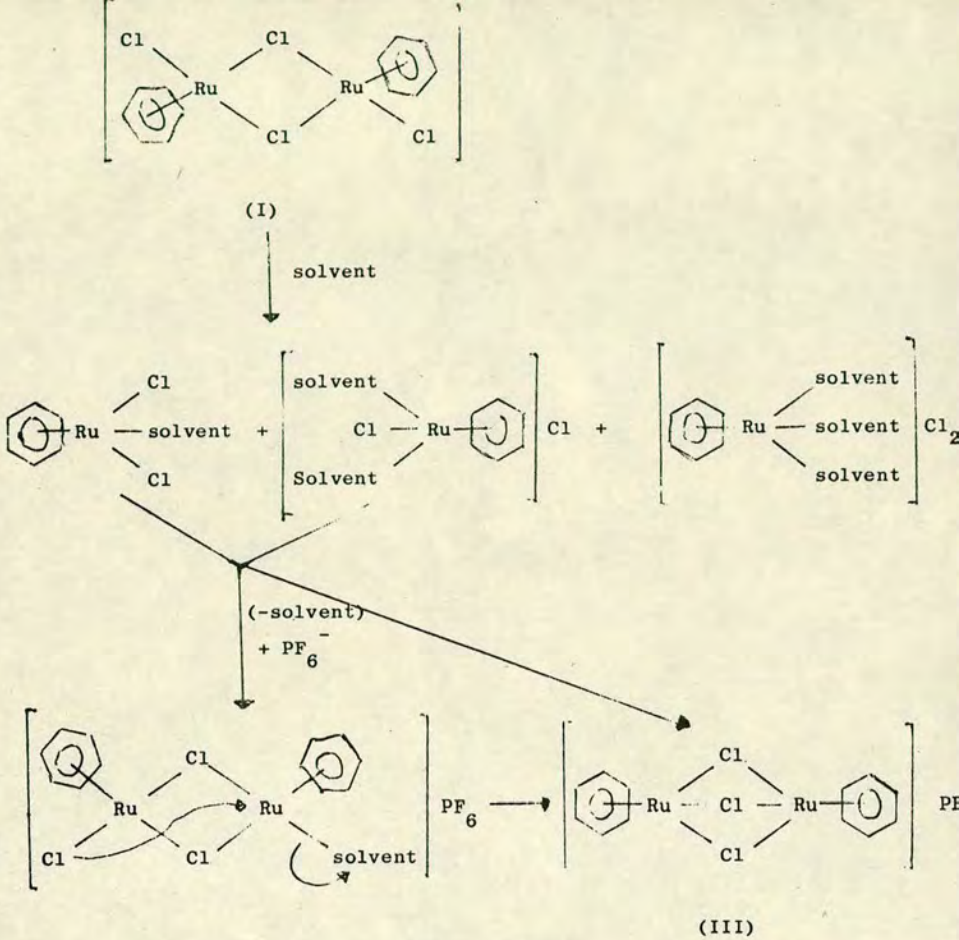
[†] Interestingly in ref [3], only a single resonance for (IIIa) in D_2O at
.04δ was reported. As discussed earlier, the difference in chemical shift
s probably due to the different references used but the observation of
nly one signal for (IIIa) in ref [3] is puzzling.



SCHEME

methanol or hot water.* These may then couple to give the triple chloride bridged cation directly, or on the basis of evidence from earlier work with ruthenium ethyldiphenylphosphinite complexes [17], via the cationic, double chloride bridged solvated intermediate $[(C_6H_6)ClRuCl_3Ru(solvent)(C_6H_6)]^+$ which then rearranges readily to (III) (Scheme).

*Unfortunately, the solubility of $[\{Ru(C_6H_6)Cl_2\}_2]$ in methanol is too low to obtain ^1H nmr evidence for the formation of methanolate monomers although, of course, there is no doubt that analogous momomeric species are readily formed in D_2O and d^6-Me_2SO.

ow solubility of the PF_6^- salt of $[Ru_2(C_6H_6)_2Cl_3]^+$ in either
nol or water, together with the desire of ruthenium (II) to
ve six strong bonds is presumably the driving force for the
nation of these intermediates.

Attempts to prepare other triple halide bridged cations $[Ru_2$-
$e)_2X_3]^+$ (arene = 1,3,5-$C_6H_3Me_3$; $X = Cl^-$; arene = C_6H_6, $X = Br^-$,
SCN^-) by reaction of $[\{Ru(arene)X_2\}_2]$ with NH_4PF_6 in methanol were
ver unsuccessful, only $[\{Ru(arene)X_2\}_2]$ being isolated from the
tion mixture. This failure probably stems from the very insoluble
re of these $[\{Ru(arene)X_2\}_2]$ compounds which prevents formation of
eciable amounts of methanolate monomers.

Reactions of $[Ru_2(C_6H_6)_2Cl_3]PF_6$

Originally, it was hoped that this high yield synthesis of
$(C_6H_6)_2Cl_3]PF_6$ (III) might provide a general route to the preparation
omplexes such as $[Ru_2Cl_3L_6]^+$ (L = C_5H_5N, Me_2SO, RCN etc) via
lacement of η^6-C_6H_6 groups. However, as discussed above, the tendency
III) to generate monomers by facile bridge cleavage proved greater than
desire to undergo replacement of the coordinated benzene rings. Thus,
uxing compound (III) with excess of pyridine in ethanol for ca 4h
an orange solution which on standing under nitrogen for a further
deposited an orange crystalline solid. On the basis of analytical
, together with ^1H nmr, ir and conductivity studies, this was best
ulated as the monomeric cation $[Ru(C_6H_6)Cl(C_5H_5N)_2]PF_6$. Concentration
he remaining filtrate gave the non-conducting orange-solid trans-
$l_2(C_5H_5N)_4]$. Attempts to retain the chloride bridges but induce
acement of η^6-C_6H_6 groups for pyridine by photolysis of the same
tion mixture also proved unsuccessful, only $[Ru(C_6H_6)Cl(C_5H_5N)_2]PF_6$
trans-$[RuCl_2(C_5H_5N)_4]$ being isolated.

Reaction between compound (III) and Et_2S gave two compounds
tified as $[Ru(C_6H_6)Cl(Et_2S)_2]PF_6$ and $[Ru(C_6H_6)Cl_2(Et_2S)]$. This
ge cleavage reaction also occurred with tertiary phosphines and

arsines when (III) was shaken in methanol with excess of the ligand for short reaction times and this provided a route to the previously unknown cationic tertiary phosphine complexes $[Ru(C_6H_6)Cl(PR_3)_2]PF_6$ (PR_3 = PPh_3, PMe_2Ph, $PMePh_2$).

The reaction of (III) with excess of PR_3 under reflux conditions sometimes produced loss of the η^6-C_6H_6 groups. For example, refluxing (III) with excess of PPh_3 in methanol gave a mixture of $[Ru(C_6H_6)Cl(PPh_3)_2]$-PF_6 and $[RuCl_2(PPh_3)_3]$. In contrast, refluxing (III) with excess of PMe_2Ph in methanol gave a yellow solution from which only the triple chloride bridged complex $[Ru_2Cl_3(PMe_2Ph)_6]PF_6$ was isolated. As discussed earlier [12,17], this cation was most likely formed by rearrangement reactions of cis-$[RuCl_2(PMe_2Ph)_4]$, itself formed by bridge cleavage and η^6-C_6H_6 displacement from (III) by PMe_2Ph.

In conclusion, although reactions of $[Ru_2(C_6H_6)_2Cl_3]PF_6$ do not provide a route to the synthesis of new triple chloride bridged cations $[Ru_2Cl_3L_6]^+$, the facile bridge cleavage reaction does give a convenient synthetic route to new η^6-C_6H_6 cationic compounds of type $[Ru(C_6H_6)ClL_2]PF_6$. Recent work has shown that similar facile bridge cleavage reactions occur with other triple chloride bridged complexes. For example, reaction of $[Ru_2YCl_4(PPh_3)_4]$ (Y = CO,CS) with excess of $P(OR)Ph_2$ (R = Me,Et) in benzene gave a mixture of $[Ru(Y)Cl_2(P(OR)Ph_2)_3]$ and $[RuCl_2(P(OR)Ph_2)_3]$[18].

In view of this, it is surprising that the closely related $[Ru_2Cl_3$-$(PR_3)_6]^+$ cations do not undergo bridge cleavage reactions with excess of PR_3 [19], although this may be a result of the strong electron donating ability of the coordinated PR_3 groups which inhibits bridge cleavage by other nucleophiles (cf the inertness of $[Ru(C_6H_6)Cl_2(PR_3)]$ compounds towards nucleophilic attack on the ring [1]).

Experimental

Microanalyses were by B.M.A.C. and the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the region 4000-250 cm^{-1} on a Perkin Elmer 457 grating spectrometer using Nujol

nd hexachlorobutadiene mulls on caesium iodide plates and in the egion 400-200 cm^{-1} on a Beckman RIIC IR 720 far ir spectrometer ing pressed polythene discs. Hydrogen-1 nmr spectra were obtained n Varian Associates HA-100 and EM-360 spectrometers and $^{13}C-\{^{1}H\}$ mr spectra on a Varian XL100 spectrometer operating at 25.2 MHz ^{13}C chemical shifts quoted in ppm to high frequency of $SiMe_4$). onductivity measurements were made at 298K using a model 310 Portland lectronics conductivity bridge. As described earlier [17], plots of $\Lambda_o - \Lambda_c$ vs $C^{\frac{1}{2}}$ gave a straight line whose slope is a function of the onic charges [20]. Melting points were determined with a Köfler hot-tage microscope and are uncorrected.

laterials

Ruthenium trichloride hydrate (Johnson Matthey); cyclohexa-1,3-diene, ammonium hexafluorophosphate and triphenylarsine (Ralph Emanuel Ltd); caesium chloride, triphenylphosphine and sodium tetraphenylborate (B.D.H.); methyldiphenylphosphine and dimethylphenylphosphine (Maybridge): nitro-ethane, pyridine, acetonitrile and mesitylene (Fisons); dimethylsulphoxide (Hopkins and Williams); triphenylstibine (Kodak). $[\{Ru(C_6H_6)Cl_2\}_2]$ and $[\{Ru(C_6H_3Me_3)Cl_2\}_2]$ were prepared as described earlier [1,3] from "$RuCl_3xH_2O$", cyclohexa-1,3-diene (or cyclohexa-1,4 diene) or 1,3,5-trimethylcyclohexa-,4-diene respectively. $[\{Ru(C_6H_6)X_2\}_2]$ (X = Br, I, SCN) were prepared y treating aqueous solutions of $[\{Ru(C_6H_6)Cl_2\}_2]$ with an excess of LiX.

Analytical and conductivity data for the various compounds are iven in Table 1 and Hydrogen-1 nmr data are listed in Table 2. Diagnostic r bands are listed for each compound. All reactions were carried out in egassed solvents under an atmosphere of nitrogen and a medium pressure, Hanovia 1L mercury U.V. lamp was used for the photochemical reaction.

Caesium(benzene)(trichloro)ruthenate(II): The compound $[\{Ru(C_6H_6)Cl_2\}_2]$ (0.20g,0.40 mmol) was shaken in ethanol (25 cm^3) with an excess of caesium chloride (0.40g) and concentrated hydrochloric acid (5 cm^3) for 5 days. The resulting orange suspension was decanted off and washed

TABLE 1

Analytical and Conductivity Data for some η^6-Areneruthenium(II) Complexes

Compound	Found %				Calculated %				Λ_m [a]
	C	H	N	Cl	C	H	N	Cl	
$Cs[Ru(C_6H_6)Cl_3]$	16.9	1.4	-	25.2	17.2	1.4	-	25.5	37.4[b]
$[Ru(C_6H_6)Cl_2(C_5H_5N)]$	40.4	3.3	4.6	-	40.1	3.3	4.3	-	
$[Ru(C_6H_6)Cl_2(PPh_3)]$	56.6	4.3	-	-	56.3	4.1	-	-	
$[Ru(C_6H_6)Cl_2(PMePh_2)]$	49.9	4.1	-	-	50.7	4.2	-	-	
$[Ru(C_6H_6)Cl_2(Me_2SO)]$	28.8	3.6	-	-	29.2	3.2	-	-	
$[RuCl_2(PMe_2Ph)_4]$	52.4	6.1	-	-	53.0	6.1	-	-	30.0[c]
$[Ru_2(C_6H_6)_2Cl_3]PF_6$	23.8	1.9	-	16.2	23.6	1.9	-	17.4	82.0
$[Ru(C_6H_6)Cl(C_5H_5N)_2]PF_6$	37.0	3.0	5.3	-	37.1	3.1	5.4	-	84.0
$[Ru(C_6H_6)Cl_2(Et_2S)]$	34.9	4.6	-	-	35.3	4.7	-	-	
$[Ru(C_6H_6)Cl(Et_2S)_2]PF_6$	31.5	4.6	-	-	31.2	4.8	-	-	64.0
$[Ru(C_6H_6)Cl(PPh_3)_2]PF_6$	56.7	4.2	-	-	57.1	4.1	-	-	78.0
$[Ru(C_6H_6)Cl(AsPh_3)_2]PF_6$	51.6	3.7	-	-	51.9	3.7	-	-	75.0
$[Ru(C_6H_6)Cl(PMe_2Ph)_2]PF_6$	41.3	4.4	-	-	41.5	4.4	-	-	72.0
$[Ru(C_6H_6)Cl(PMePh_2)_2]PF_6$	50.5	4.8	-	-	50.6	4.2	-	-	67.0
$[Ru_2Cl_3(PMe_2Ph)_6]PF_6$	44.9	5.1	-	-	44.9	5.2	-	-	74.0
$[Ru(NH_3)_2(C_6H_6)Cl]_3(PF_6)_3 \cdot NH_4PF_6$	16.3	2.9	7.1	-	16.1	3.0	7.3	-	

[a] Equivalent conductivities (S cm^2 mol^{-1}) measured in nitromethane (unless stated) at 10^{-3} mol dm^{-3} concentration [b] measured in H_2O [c] measured in CH_2Cl_2 - rearranges to $[Ru_2Cl_3(PMe_2Ph)_6]Cl$.

with methanol and diethyl ether mp. 270°C (decomp) (Yield 0.31g,95%) ν(RuCl) 280 (broad) cm^{-1}.

Benzene(dichloro)pyridine ruthenium(II): The compound $Cs[Ru(C_6H_6)Cl_3]$ (0.10g;0.23 mmol) was shaken in methanol (10 cm^3) with excess of pyridine (1.0 cm^3) for ca 4h. Concentration of the resulting yellow solution and addition of diethyl ether gave an orange solid mp. 245°C (decomp) (0.07g, 86%) ν(RuCl) 280 cm^{-1}.

ogen-1 nmr data for some η^6-Areneruthenium(II) Complexes

Compound	Solvent	δ[a] ppm η^6-C_6H_6	other resonances
$(C_6H_6)Cl_2\}_2]$	D_2O[b]	6.39[c];6.50[c]	
$u(C_6H_6)Cl_3]$	D_2O[b]	6.40[c]	
$C_6H_6)Cl_2(C_5H_5N)]$	d^6-Me_2SO	5.65,5.90[d]	7.30,8.80(pyridine)
$C_6H_6)Cl_2(Me_2SO)]$	$CDCl_3$	5.90	ca 2.70(br) (Me_2SO)
$C_6H_6)Cl_2PPh_3]$	$CDCl_3$	5.40	7.50 (PPh_3)
$C_6H_6)Cl_2(PMePh_2)]$	$CDCl_3$	5.40	7.65(Ph);1.95(d)($^2J_{PH}$ 12.0Hz) (Me)
$C_6H_6)Cl_2(PMe_2Ph)]$	$CDCl_3$	5.35	7.50(Ph);1.85(d)($^2J_{PH}$ 12.0Hz) (Me)
	$CDCl_3$[b]	5.95	8.03(Ph);2.48(d)($^2J_{PH}$ 12.0Hz) (Me)
$(C_6H_6)Cl_2(SbPh_3)]$	$CDCl_3$	5.68	7.40-7.70($SbPh_3$)
$(C_6H_6)Cl_2(AsPh_3)]$	$CDCl_3$	5.50	7.40-7.60($AsPh_3$)
$(C_6H_6)Cl_2(Et_2S)]$	$CDCl_3$	5.70	2.90(q);1.35(t) (Et_2S)
$_2(C_6H_6)_2Cl_3]PF_6$	d^3-$MeNO_2$	5.90	
	D_2O[b]	6.35[c],6.48[c]	
	d^6-Me_2SO	5.95[c],6.15[c],6.50[c]	
$(C_6H_6)Cl(C_5H_5N)_2]PF_6$	d^6-Me_2CO	6.16	7.45,8.00,8.85(pyridine)
$(C_6H_6)Cl(Et_2S)_2]PF_6$	$CDCl_3$	5.95	3.00(q);1.45(t) (Et_2S)
$(C_6H_6)Cl(PPh_3)_2]PF_6$	$CDCl_3$	5.52	7.30(PPh_3)
$(C_6H_6)Cl(PMePh_2)_2]PF_6$	$CDCl_3$	5.75	7.20-7.60(Ph) 1.60(t) (Me)
$(C_6H_6)Cl(PMe_2Ph)_2]PF_6$	$CDCl_3$	5.87	7.50(Ph);1.64(t);2.12(t)(Me)
$(C_6H_6)Cl(AsPh_3)_2]PF_6$	$CDCl_3$	5.66	7.40-7.60($AsPh_3$)

(doublet), t (triplet), q (quartet)

Unless specified, reference is TMS(internal lock) [b] With respect to

ternal TMS capillary. [c] See text for assignment of these resonances

From [$Ru(C_6H_6)Cl_2(d^6$-$Me_2SO)$]

Benzene(dichloro)triphenylphosphine ruthenium(II): The compound $Cs[Ru(C_6H_6)Cl_3]$ (0.10g; 0.23 mmol) was shaken with excess of PPh_3 (0.10g; 0.40 mmol) in methanol for ca 3h to give a dark red crystalline solid mp. 182°C (0.11g,91%) ν(RuCl) 295, 280 cm^{-1}.

Benzene(dichloro)methyldiphenylphosphine ruthenium(II): mp. 197°C (0.09g,82%) ν(RuCl) 290, 270 cm^{-1}; benzene(dichloro)dimethylphenylphosphine-ruthenium(II) mp. 175°C (0.07g; 78%) ν(RuCl) 290, 275 cm^{-1}; benzene-(dichloro)triphenylstibine ruthenium(II) mp. 220-222°C ν(RuCl) 290, 269 cm^{-1} and benzene(dichloro)dimethylsulphoxide ruthenium(II) mp. 211°C ν(RuCl) 291, 272 cm^{-1} were similarly prepared.

Cis-dichlorotetrakis(dimethylphenylphosphine)ruthenium(II): The compound $Cs[Ru(C_6H_6)Cl_3]$ (0.10g; 0.23 mmol) was refluxed in methanol with excess PMe_2Ph (0.50 cm^3) for 6h. The resulting yellow solution on standing gave a yellow, crystalline solid mp. 126°C (0.13g; 82%) ν(RuCl) 288, 241 cm^{-1}.

Tri-μ-chlorobis[(benzene)ruthenium(II)]hexafluorophosphate:- Method A: The complex $[\{Ru(C_6H_6)Cl_2\}_2]$ (0.20g; 0.40 mmol) was heated under reflux with water (10 cm^3) for 2h. The orange solution was filtered and treated with a saturated aqueous solution of NH_4PF_6. After several days the orange precipitate was filtered off and washed with water and methanol mp. 255°C (decomp) (0.03g; 12%). On leaving the filtrate for another 7 days, another orange crystalline solid was deposited which was characterised by X-ray analysis [14] as $[Ru(NH_3)_2(C_6H_6)Cl]_3(PF_6)_3.NH_4PF_6$ (νRuCl 285 cm^{-1}; ν(NH) 3180, 3250, 3320, 3370 cm^{-1}; δ(NH) 1615, 1630 cm^{-1}; ν(Ru-N) 421, 440, 455 cm^{-1}). Unfortunately, subsequent attempts to prepare this latter compound were unsuccessful.

Method B: The complex $[\{Ru(C_6H_6)Cl_2\}_2]$ (0.20g; 0.40 mmol) was stirred in methanol (25 cm^3) with excess of NH_4PF_6 (0.16g; 1.00 mmol) for 24h. The orange-yellow solid was filtered off and washed with water, methanol and diethyl ether mp. 280°C (decomp) (0.22g; 90%) ν(RuCl) 264, 276 cm^{-1}. Conductivity in $MeNO_2$ at 298K. Slope of $\Lambda_o - \Lambda_c$ vs $C^{\frac{1}{2}}$ plot = 207; for $[Ru_2Cl_3(PMe_2Ph)_6]PF_6$, slope = 190. $^{13}C-\{^1H\}$nmr in d^3-$MeNO_2$ at 303K.

ppm (singlet). The compound is insoluble in $CHCl_3$, CH_2Cl_2, benzene
very sparingly soluble in acetone.

ene(chloro)bis(pyridine)ruthenium(II)hexafluorophosphate: The complex
$(C_6H_6)_2Cl_3]PF_6$ (0.09g; 0.14 mmol) was refluxed in ethanol (30 cm^3)
pyridine (0.40 cm^3) for ca 6h. The yellow solution on standing for
gave a yellow crystalline solid mp. 227-229°C (0.05g; 66%) ν(RuCl)
cm^{-1}. Concentration of the filtrate from this reaction gave an
ge solid trans-dichlorotetrakis(pyridine)ruthenium(II) mp. 255°C (decomp)
03g; 24%) ν(RuCl) 338 cm^{-1}.

zenedichloro(diethylsulphide)ruthenium(II): The complex $[Ru_2(C_6H_6)_2$-
$]PF_6$ (0.10g; 0.16 mmol) was refluxed in ethanol (30 cm^3) with Et_2S-
20 cm^3) for ca 3h. The orange solution was filtered and concentrated
evaporation of solvent under vacuo. The orange precipitate obtained
recrystallised from acetone/diethyl ether mp. 225°C (decomp) ν(RuCl)
, 265 cm^{-1}). The filtrate from the above reaction gave an orange
stalline solid on standing for 24h identified as benzene(chloro)bis-
ethylsulphide)ruthenium(II)hexafluorophosphate mp. 175°C, ν(RuCl)
cm^{-1}.

zenechlorobis(triphenylphosphine)ruthenium(II)hexafluorophosphate:
complex $[Ru_2(C_6H_6)_2Cl_3]PF_6$ (0.20g; 0.32 mmol) was shaken in methanol
cm^3) with excess of PPh_3 (0.20g; 0.80 mmol). The red precipitate
filtered off from the yellow solution, recrystallised from CH_2Cl_2/
ane and identified as $[Ru(C_6H_6)Cl_2(PPh_3)]$. Addition of diethylether
hexane to the yellow filtrate gave the yellow crystalline product
172°C (0.11g, 41%), ν(RuCl) 290 cm^{-1}. Similar reactions gave the
low solids benzenechlorobis(triphenylarsine)ruthenium(II)hexafluoro-
osphate mp. 142°C, ν(RuCl) 310 cm^{-1}; benzenechlorobis(methyldiphenyl-
osphine)ruthenium(II)hexafluorophosphate mp. 158°C ν(RuCl) 292 cm^{-1}
d benzenechlorobis(dimethylphenylphosphine)ruthenium(II)hexafluoro-
osphate mp.209-211°C, ν(RuCl) 298 cm^{-1}.

Tri-μ-chlorobis[tris(dimethylphenylphosphine)ruthenium(II)] hexafluorophosphat

The compound $[Ru_2(C_6H_6)_2Cl_3]PF_6$ (0.20g; 0.32 mmol) was refluxed in methanol (20 cm^3) with excess of PMe_2Ph (1 cm^3) for 5h. Addition of diethyl ether to the yellow solution gave a yellow crystalline solid mp. 238-239°C (0.37g, 92%).

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Preliminary communication

A CONVENIENT SYNTHETIC ROUTE TO TRIPLE HALIDE BRIDGED ARENE COMPLEXES OF RUTHENIUM(II) AND OSMIUM(II)

T. ARTHUR and T.A. STEPHENSON*

Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ (Great Britain)

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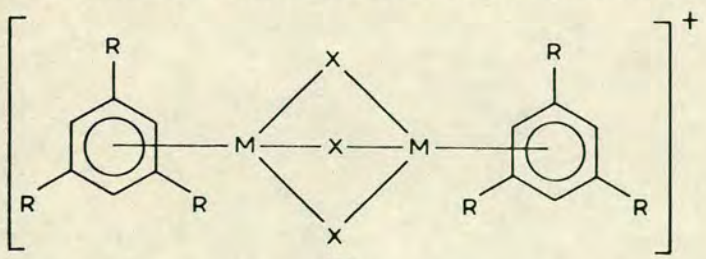
Summary

Protonation with HBF_4 of equimolar mixtures of $[M(arene)X_2(C_5H_5N)]$ and $[M(arene)X(C_5H_5N)_2]PF_6$ in methanol provides a convenient, high yield, synthetic route to the triple halide bridged arene complexes $[M_2(arene)_2X_3]BF_4$ (M = Ru; X = Cl, Br; arene = C_6H_6, 1,3,5-$C_6H_3Me_3$; M = Os, X = Cl, arene = C_6H_6).

Recently we reported that reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ in methanol at ambient temperature with a slight excess of NH_4PF_6 for 24 h gave, in high yield, $[(\eta\text{-}C_6H_6)RuCl_3Ru(\eta\text{-}C_6H_6)]PF_6$. The most likely mechanism of formation of this cation was proposed to be by intermolecular coupling of the weakly solvated monomers $[Ru(C_6H_6)Cl_2(MeOH)]$ and $[Ru(C_6H_6)Cl(MeOH)_2]^+$. Unfortunately, attempts to prepare other triple halide bridged arene cations by reaction of the appropriate double halide bridged dimers with NH_4PF_6 in methanol were unsuccessful, probably because of the very insoluble nature of these $[\{Ru(arene)X_2\}_2]$ compounds [1].

We now wish to report a more convenient, high yield, synthetic route to these $[M_2(arene)_2X_3]^+$ cations (I). This involves the formation in situ of high equi-

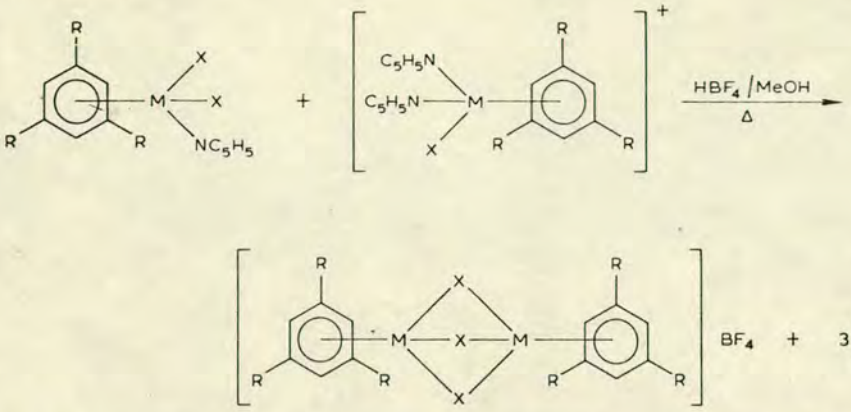


(I)

M = Ru, X = Cl, Br; R = H or Me

M = Os, X = Cl; R = H

molar concentrations of the solvated monomers $[M(arene)X_2(MeOH)]$ and $[M(arene)X(MeOH)_2]^+$ by protonation in methanol of the corresponding pyridine complexes $[M(arene)X_2(C_5H_5N)]$ and $[M(arene)X(C_5H_5N)_2]PF_6$ respectively.



Thus, for example, treatment of equimolar amounts of $[Ru(C_6H_6)Cl_2(C_5H_5N)]$ [2] and $[Ru(C_6H_6)Cl(C_5H_5N)_2]PF_6$ [1,3] in methanol with a slight excess of HBF_4 gave, after gently refluxing the solution for one hour, an almost quantitative yield of $[Ru_2(C_6H_6)_2Cl_3]BF_4$. Similarly, reaction of $[Ru(C_6H_6)Br_2(C_5H_5N)]$ and $[Ru(C_6H_6)Br(C_5H_5N)_2]PF_6$ [3] with HBF_4 gave $[Ru_2(C_6H_6)_2Br_3]BF_4$ and analogous reactions with the appropriate pyridine monomers gave $[Ru_2(C_6H_3Me_3)_2X_3]BF_4$ (X = Cl, Br).

As observed earlier for the $[Ru_2(C_6H_6)_2Cl_3]^+$ cation [1], all these compounds undergo facile bridge cleavage reactions in solvents such as H_2O and Me_2SO, but fortunately, they are all soluble and stable in CH_3NO_2. Thus, ^1H and ^{13}C-$\{^1H\}$ NMR studies in CD_3NO_2 (Table 1) together with analytical data, conductivity (all 1/1 electrolytes) and far infrared studies (only bridging ν(RuX) present) establish unequivocally the structure of the compounds.

In an attempt to make the mixed bridge compound $[(C_6H_6)RuCl_2BrRu(C_6H_6)]$-$BF_4$, equimolar amounts of $[Ru(C_6H_6)Cl_2(C_5H_5N)]$ and $[Ru(C_6H_6)Br(C_5H_5N)_2]$-$PF_6$ were treated with HBF_4/MeOH. However, although the product analysed closely for "$[Ru_2(C_6H_6)_2Cl_2Br]BF_4$", its ^1H NMR spectrum in CD_3NO_2 showed

TABLE 1

^1H AND ^{13}C-$\{^1H\}$ NMR SPECTRA IN CD_3NO_2 OF SOME RUTHENIUM(II) AND OSMIUM(II) ARENE COMPLEXES

Compound	^1H[a]	^{13}C-^1H [a]
$[Ru_2(C_6H_6)_2Cl_3]BF_4$	5.944	82.04
$[Ru_2(C_6H_6)_2Br_3]BF_4$	5.922	82.37
"$[Ru_2(C_6H_6)_2Cl_2Br]BF_4$" } "$[Ru_2(C_6H_6)_2ClBr_2]BF_4$" }	5.944,5.937,5.929,5.922	—
$[Os_2(C_6H_6)_2Cl_3]BF_4$	6.64	73.55
$[RuOs(C_6H_6)_2Cl_3]BF_4$	6.46,6.06	82.21,73.82
$[Ru_2(C_6H_3Me_3)_2Cl_3]BF_4$	5.35(H),2.22(Me)	102.01(CMe),75.72(CH),19.42(Me)
$[Ru_2(C_6H_6)(C_6H_3Me_3)Cl_3]BF_4$	5.92,5.37(H),2.20(Me)	102.01(CMe),82.02,75.89(CH),19.28(Me)

[a] Reference is $(CH_3)_4Si$; all singlets.

four η-C_6H_6 resonances at 5.944, 5.937, 5.929 and 5.922 ppm of relative intensity 8/12/6/1. The resonance at δ 5.944 ppm arises from $[Ru_2(C_6H_6)_2Cl_3]BF_4$ and that at δ 5.922 ppm from $[Ru_2(C_6H_6)_2Br_3]BF_4$. Conversely, reaction of $[Ru(C_6H_6)Br_2(C_5H_5N)]$ and $[Ru(C_6H_6)Cl(C_5H_5N)_2]PF_6$ (1/1 molar ratio) with HBF_4/MeOH gave a product analysing for "$[Ru_2(C_6H_6)_2ClBr_2]BF_4$" which showed the same four ^{1}H NMR η-C_6H_6 resonances but now with relative intensities 1/6/12/8. Thus, these experiments clearly show that statistical mixtures of $[Ru_2(C_6H_6)_2Cl_3]^+$, $[Ru_2(C_6H_6)_2Cl_2Br]^+$, $[Ru_2(C_6H_6)_2ClBr_2]^+$ and $[Ru_2(C_6H_6)_2Br_3]^+$ and $[Ru_2(C_6H_6)_2Br_3]^+$ cations are formed in these reactions.

It is readily demonstrated that this facile halide exchange can occur prior to protonation since on mixing $[Ru(C_6H_6)Cl_2(PPh_3)]$ * and $[Ru(C_6H_6)Br(C_5H_5N)_2]^+$ in acetone-d_6, ^{1}H NMR studies reveal that some $[Ru(C_6H_6)Br_2(PPh_3)]$ and $[Ru(C_6H_6)Cl(C_5H_5N)_2]^+$ are rapidly formed. However, the ^{1}H NMR spectrum of a mixture of $[Ru_2(C_6H_6)_2Cl_3]BF_4$ and $[Ru_2(C_6H_6)_2Br_3]BF_4$ in CD_3NO_2 after several minutes at ambient temperature shows four η-C_6H_6 resonances, indicating that facile halide exchange can also occur after formation of the dimers (cf. the formation of some $[PdPtCl_4L_2]$ from reaction of $[Pd_2Cl_4L_2]$ and $[Pt_2Cl_4L_2]$ [4]).

In an attempt to synthesise the tetrameric cation $[\{Ru(C_6H_6)Cl\}_4]^{4+}$ a suspension of $[Ru(C_6H_6)Cl(C_5H_5N)_2]PF_6$ in methanol was treated with HBF_4 but the only product isolated was $[Ru_2(C_6H_6)_2Cl_3]BF_4$ in low yield (ca. 25%). This clearly demonstrates that protonation removes some coordinated chloride as HCl which then reacts to form some $[Ru(C_6H_6)Cl_2MeOH]$. Similarly, protonation of $[Os(C_6H_6)Cl(C_5H_5N)_2]PF_6$ [3] gave $[Os_2(C_6H_6)_2Cl_3]BF_4$ whereas treatment of an equimolar mixture of $[Ru(C_6H_6)Cl_2(C_5H_5N)]$ and $[Os(C_6H_6)Cl(C_5H_5N)_2]PF_6$ with HBF_4/MeOH gave a statistical mixture of $[Ru_2(C_6H_6)_2Cl_3]BF_4$, $[Os_2(C_6H_6)_2Cl_3]BF_4$ and $[RuOs(C_6H_6)_2Cl_3]BF_4$. Mixing the pure ruthenium and osmium dimers at ambient temperature in CD_3NO_2 rapidly gave some $[RuOs(C_6H_6)_2Cl_3]^+$ cation.

Finally, using these methods, the $[(C_6H_6)RuCl_3Ru(C_6H_3Me_3)]^+$ cation can be generated, but not separated, from the $[Ru_2(C_6H_6)_2Cl_3]^+$ and $[Ru_2(C_6H_3Me_3)_2Cl_3]^+$ cations.

Acknowledgement

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*$[Ru(C_6H_6)Cl_2PPh_3]$ was used because of the insolubility of $[Ru(C_6H_6)Cl_2(C_5H_5N)]$ in acetone.

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Preliminary communication

Electrochemical Studies on Neutral Triple-Bridged Di-Ruthenium Compounds.

by T. Arthur, R. Contreras, G.A. Heath,* G. Hefter,†
A.J. Lindsay, D.J.A. Riach and T.A. Stephenson.*
Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, Scotland.

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Summary

Voltammetric studies reveal that, like $[Ru_2Cl_4(PPh_3)_4(CO)]$, triply-bridged complexes $[Ru_2Cl_4L_5]$ (L = $PClPh_2$, $PMePh_2$, PEt_2Ph) are reversibly oxidized to $[Ru_2Cl_4L_5]^+$. The mixed valence complexes $[Ru_2Cl_5L_3Y]$ (L = PPh_3, $P(tol)_3$; Y = CO, CS) undergo a corresponding reduction to $[Ru_2Cl_5L_3Y]^-$; whereas $[Ru_2Cl_5L_4]$ (L = PEt_2Ph, $As(tol)_3$) and $[Ru_2Cl_6(AsPh_3)_3]$ are both reduced and oxidised in reversible one-electron steps. For the bridging $(RuCl_3Ru)^{z+}$ moiety, the redox series z = 1, 2, 3, 4 is established.

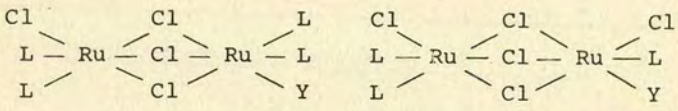
Recently we drew attention to the fact that the known triply-chloro-bridged di-ruthenium complexes range in oxidation level from di-Ru(II) to di-Ru(III) systems, suggesting the possibility of stepwise bridge-based

†present address, Department of Chemistry, University of Malaya, Kualalumpur, Malaysia.

redox equilibria (equation 1), and went on to report the reversible one-electron oxidation of $[Ru_2Cl_4(PPh_3)_4(CO)]$ and its analogues (I) to the corresponding mixed valence cations [1].

$$(RuCl_3Ru)^{+} \rightleftharpoons (RuCl_3Ru)^{2+} \rightleftharpoons (RuCl_3Ru)^{3+} \qquad (1)$$

New voltammetric studies at a platinum electrode in CH_2Cl_2 establish that complexes $[Ru_2Cl_4(PR_3)_5]$ (II) likewise undergo a single reversible one-electron oxidation in the accessible potential range.† The electrode potential is seen to be markedly dependent on the nature of the phosphine (Table) with the more basic phosphines promoting readier oxidation.



I II III IV

I L = PPh_3, $Ptol_3$; Y = CO, CS

II L = Y = $PClPh_2$, $PMePh_2$, PEt_2Ph

III L = PPh_3, $Ptol_3$; Y = CO, CS

IV L = Y = PEt_2Ph, $Astol_3$

Neutral mixed-valence complexes $[Ru_2Cl_5L_4]$, where L represents a soft neutral ligand, should offer the best opportunity for observing both redox steps within one molecule [1], and earlier synthetic work provides a systematic route to such compounds through HCl treatment

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†All the 'reversible' waves reported here satisfy the appropriate criteria of diffusion controlled electrode reversibility on Pt for cyclic voltammetry (CV) and alternating current voltammetry (acV) over widely varying CV scan rate ν(50-500mVsec^{-1}), and acV frequency ω (20-400Hz). Thus ΔE_{pp}(CV) ~ 60mV, $i_c = i_a \propto \nu^{\frac{1}{2}}$, $E_{\frac{1}{2}}$(CV) $= E_p$(acV), i_p(acV) $\propto \omega^{\frac{1}{2}}$.

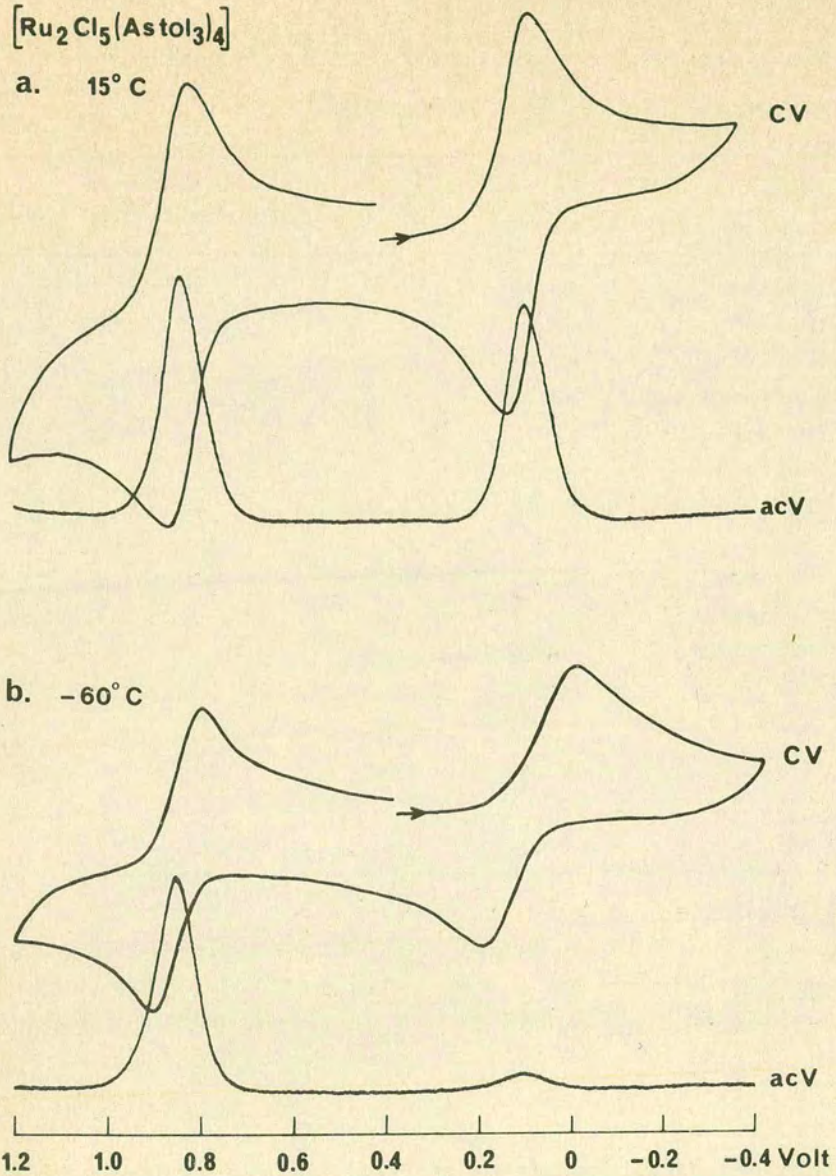

Fig. 1. Voltammetry of $[Ru_2Cl_5(Astol_3)_4]$ vs Ag/AgI in CH_2Cl_2: a) at 15°C, b) at -60°C.

of $[Ru_2Cl_4L_5]$ [2]. Accordingly, $[Ru_2Cl_5(PPh_3)_3(CS)]$ and its analogues (III) were examined and found to undergo a reversible one-electron reduction to the corresponding di-Ru(II) mono-anion (Table). However, in these compounds

TABLE

Reversible Electrode Potentials for Binuclear Ruthenium Complexes

$E_{\frac{1}{2}}$ (volts) at 20°C in CH_2Cl_2/0.5M Bu_4NBF_4[a]

Complex	II,II/II,III	II,III/III,III	III,III/III,IV
$[Ru_2Cl_4(CO)(PPh_3)_4]$	+0.75		
$[Ru_2Cl_4(CS)(PPh_3)_4]$	+0.74		
$[Ru_2Cl_4(CO)(Ptol_3)_4]$	+0.65		
$[Ru_2Cl_4(CS)(Ptol_3)_4]$	+0.64		
$[Ru_2Cl_4(PClPh_2)_5]$	+1.20		
$[Ru_2Cl_4(PMePh_2)_5]$	+0.75		
$[Ru_2Cl_4(PEt_2Ph)_5]$	+0.47		
$[Ru_2Cl_5(CO)(PPh_3)_3]$	+0.03		
$[Ru_2Cl_5(CS)(PPh_3)_3]$	+0.02		
$[Ru_2Cl_5(CO)(Ptol_3)_3]$	-0.06		
$[Ru_2Cl_5(PEt_2Ph)_4]$	-0.28	+1.27	
$[Ru_2Cl_5(Astol_3)_4]$	+0.10	+0.83	
$[Ru_2Cl_6(AsPh_3)_3]$		-0.37	+0.67

[a] versus a Ag/AgI/0.5M Bu_4NBF_4/CH_2Cl_2 reference electrode, at which ferrocene is oxidized at +0.60V. This electrode is shifted by 0.2V w.r.t. the Bu_4NClO_4-containing electrode used previously[1].

the anticipated anodic couple is not observed before the onset of multi-electron oxidation at extreme potentials.

In contrast, the symmetrical complexes (IV) exhibit one-electron reduction and oxidation steps which are both reversible in CH_2Cl_2 at room temperature (Table, Figure 1a), thus providing the first clear example of the predicted stepwise redox equilibria. Complementary studies on oxidation of harder systems such as $[Ru_2Cl_3(H_2O)_6]^{3+}$

and $[Ru_2Cl_3(NH_3)_6]^{3+}$ have been reported [3,4]. Interestingly, the measured separation of the two couples is very wide (~1.5V) for $[Ru_2Cl_5(PEt_2Ph)_4]$ whereas both couples occur at relatively modest potentials in $[Ru_2Cl_5(Astol_3)_4]$, implying that the coordinated arsine facilitates both oxidation and reduction. Intuitively this versatility is appropriate for the more polarisable π-acid ligand.

Voltammetry of the related di-Ru(III) complex $[Ru_2Cl_6(AsPh_3)_3]$ reveals a single reversible one-electron reduction. Further reduction would not be expected in the available cathodic range. Remarkably however, $[Ru_2Cl_6(AsPh_3)_3]$ also shows a reversible one-electron oxidation to form a unique Ru(III)/Ru(IV) binuclear cation, extending the sequence of equation 1. These observations have prompted a comparative study on monomeric ruthenium complexes which is reported separately [5]. Among the binuclear compounds of varying stoichiometry, replacement of a neutral ligand by Cl^- is accompanied by a shift of roughly -0.7V in the II,III/III,III redox couple.

The structural and spectroscopic changes accompanying stepwise electron-transfer in the bridged complexes are of considerable interest, expecially since it seems that the degree of metal-metal interaction in 35e and 34e systems may vary in apparently analogous complexes, depending on the identity of the bridging groups and terminal ligands. Strikingly, low temperature voltammetric studies on $[Ru_2Cl_5(Astol_3)_4]$ show that at -40°C the cathodic couple involves slow charge-transfer at the electrode although the anodic couple remains fully reversible (Figure 1b). A sluggish structural rearrangement accompanying the reduction is

implied and it is exciting to speculate that this might be related to loss of a metal-metal bond. Preliminary controlled potential electrosyntheses confirm the indefinite stability of species such as $[Ru_2Cl_4(PPh_3)_4(CO)]^+$ and $[Ru_2Cl_5(Astol_3)_4]^-$ at low temperature and work in this area is continuing.

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